NBS MONOGRAPH 40

Thermocouple Materials

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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Thermocouple Materials

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National Bureau of Standards Monograph 40

Issued March 1, 1962

Reprinted with corrections, February 1969

For sale by the Superintendent of Documents, U.S. Government Printing Office
Washington, D.C. 20402 - Price 50 cents

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Thermocouple Materials *

F. R. Caldwell

Thermocouple materials are considered that are used primarily as immersion temperature sensors in the range from 0 °C up. Included are the conventional thermocouples that have survived since the beginnings of the art of thermoelectric temperature measurement, newer noble metal thermocouples, and thermocouples of refractory metals for use in the extreme range for immersed sensors. Thermocouples for thermoelectric generators are not considered, nor are the types commonly used chiefly in radiation receivers such as those containing antimony, bismuth, and their alloys. Because of the wide use and increasing popularity of ceramic-packed thermocouples in metal sheaths, they are included.

Limitations of the thermocouple wires are given as to range, stability, environment including atmosphere, magnitude of thermoelectric emf, and accuracy of commercially available materials of standard and extra quality. In addition, properties of the separate elements that are pertinent to the selection or use of thermocouples have been compiled. Among these are: chemical behavior, mechanical properties, specific heat, density, thermal conductivity, thermal coefficient of expansion, emissivity, electrical resistivity, and magnetic and catalytic properties.

In the case of the ceramic-packed thermocouples the following properties are presented: temperature range of the sheath, mechanical properties of the sheath, kinds of packed insulation, resistance between thermocouple wires and between wires and sheath, minimum bending radius of the packed stock, gas-tightness of the packed insulation, and types of measuring junctions available, i.e., grounded, ungrounded, bare, totally enclosed, stagnation mounting, etc.

Not all of the above information is presented for all thermocouples, but all that is readily available in the general literature, catalogs, and by private communication is included. Limitations on use of thermocouples normally are given in the text, and properties of the materials generally are presented in tables.

1. Introduction

Of the infinite combinations of metals, alloys, semiconductors, and nonmetals that can be combined to form thermocouples, only a few have found use as temperature sensors. The thermocouples that have been in common use for fifty years and more are still predominant, although some special-purpose thermocouples have appeared from time to time. Because of the needs of the jet-engine, reactor, and rocket technologies in the higher temperature ranges, however, new thermocouples are being developed to meet these recent requirements.

The purpose of this paper is to present information on materials that are used from 0 °C up in thermocouples intended primarily as immersed temperature sensors, and to give so far as is practical properties of these materials that might affect their use in temperature measurement. This information is provided with the hope that the advantages and limitations given for the various thermocouples and materials will be of value to those selecting sensors for particular uses, and that the effort now required in finding needed properties will be reduced. The material included is from many sources including catalogs, personal communications on work done at various laboratories, and the general literature. Thermoelectric generators are not considered, nor are thermocouples included of the types commonly used in radiation receivers, such as those of antimony, bismuth and their alloys.

Originally this paper was planned to cover only bare, unmounted thermocouple elements, but because of the wide and increasing use of ceramic-packed thermocouples, the latter have been included. Because the same wires are used in both kinds of thermocouples, emphasis on the ceramic-packed type will be directed chiefly toward properties of the sheath and insulation. Justification for inclusion of these properties of the ceramic-packed thermocouples and not of insulators for the bare-wire thermocouples may be thought by some to be tenuous, but it arises from consideration of the packed stock along with bare wires as thermocouple raw material.

Among factors to be considered in selection of a thermocouple as an immersed temperature sensor for a particular use may be for the thermocouple combination:

- Temperature-emf relationship
- Temperature range of use
- Diameters of wires available, and

For the separate thermocouple elements:

- Melting point
- Effects of environment on thermoelectric and mechanical properties
- Chemical properties and behavior
- Mechanical properties
- Specific heat
- Density
- Thermal conductivity
- Thermal coefficient of expansion
- Emissivity, spectral and total, of bright and oxidized surfaces

* This paper was presented at the Fourth Symposium on Temperature, Its Measurement and Control in Science and Industry; Columbus, Ohio; March 27-31, 1961; sponsored by the American Institute of Physics, the Instrument Society of America, and the National Bureau of Standards. The proceedings will be published in book form by the Reinhold Publishing Corporation, New York, N.Y.

Electrical resistivity
Temperature coefficient of resistance, and
Magnetic properties.

Not all of the properties are available for all thermocouples presented, but all that are readily accessible will be given.

In the case of the ceramic-packed stock the foregoing properties are just as important as for bare thermocouples; and in addition, some other factors must be taken into account, such as:

Temperature range of the sheath
Mechanical properties of the sheath
Kinds of packed insulation
Resistance between wires, and between wires and sheath
Minimum bending radius of the packed stock
Gas-tightness of the packed insulation, and
Types of measuring junctions available, i.e. grounded, ungrounded, bare, totally enclosed, stagnation mounting, etc.

References are made by numbers in the text to corresponding numbers of entries in the Bibliography Section. No attempt has been made to provide complete coverage of the literature, and omission of a title from the list of references is not intended as an implication of any inadequacy of the paper. References have been chosen in some cases which give broader coverage and thus provide, it is believed, greater consistency between results than might be found in similar data on the same subject from several sources. Some sacrifice of accuracy might occur occasionally because of such choices; but since many of the data are found without much, if any, information on how they were obtained, evaluation of experimental results is difficult in many cases.

The exhaustive work of Potts and McElroy [77] [1] unfortunately was received after this paper was nearly completed, and time did not permit revision to include or even properly refer to their results. It is, however, an extremely fertile source of information on base-metal thermocouples, especially ISA type K, and is recommended as excellent reference material.

No history of the thermocouple art is presented. This is considered superfluous here, because such information has been published many times in recent years, and may be expected to continue to appear in introductions of papers of the future. It is assumed throughout this paper that the reader is familiar with the basic principles of thermoelectric thermometry to the extent, at least, that he can intelligently apply them to practice.

Temperatures referred to throughout the discussions that follow are, unless otherwise indicated, in degrees C of the International Temperature Scale of 1948. In all cases where equations containing temperature are taken from a reference, they are unchanged; no adjustments have been made in them to account for the difference between the 1948 temperature scale and that used at the time of the particular work cited. In some cases, though, slight adjustments have been made on tabulated data to put them on the 1948 scale. Generally the information is given in the same units as those used by the authors, although conversion to more familiar units has been made in some cases. This may lead to some confusion, but this is thought to be only a minor disadvantage to those having interests that involve the data presented. The electromotive forces (emfs) are in terms of the absolute volt.

2. Bare Thermocouple Wires

The materials considered in this section are, for convenience, classified as follows:

1. Noble Metals
2. Base Metals
3. Refractory Metals
4. Carbon and Carbides

The first two items represent the vast majority of thermocouples now in use, and much information on them is available. Fewer data are available on the third item, but a considerable effort is being exerted in the field of refractory metals to meet the high-temperature needs of recent technological developments. Relatively little work has been done on materials of the fourth item, but some thermocouples employing graphite, carbon and carbides are used. Sufficient promise has been shown by these materials though, to make them worthy of inclusion.

Discussions of various thermocouple materials follow.

2.1. Noble Metals

a. Platinum and Platinum-Rhodium Alloys

The oldest and most used noble-metal thermocouple is the platinum-rhodium [2] versus platinum thermocouple. Both the 10 percent (ISA type S) [1] and 13 percent (ISA type R) [1] rhodium-platinum positive elements are used extensively, and the platinum-rhodium 10 percent versus platinum thermocouple continues to serve as a means of realization of and interpolation on the International Temperature Scale of 1948. More space will be devoted to these thermocouples for two reasons. First, they, in defining the temperature scale, are of more basic importance than are others, and secondly, more information is available on them than on most others.

Thermocouples having both legs of alloys of platinum and rhodium have been proposed, and some of these combinations are tabulated below.

[1] Figures in brackets indicate the literature references on page 39.
[2] When mentioning a thermocouple, the positive element is given first. This is in line with an apparent effort to standardize nomenclature among users of thermocouples.

Positive wire	Negative wire
Platinum-rhodium 13 percent.	Platinum-rhodium 1 percent.
Platinum-rhodium 20 percent.	Platinum-rhodium 5 percent.
Platinum-rhodium 30 percent.	Platinum-rhodium 6 percent.
Platinum-rhodium 40 percent.	Platinum-rhodium 20 percent.

Advantages of the all-alloy thermocouples are said to be greater stability, a somewhat greater temperature range of use, and increased stiffness with greater resistance to mechanical deterioration. The most prominent of the tabulated combinations appears to be the platinum-rhodium 30 percent versus platinum-rhodium 6 percent (30–6) thermocouple, and it will be discussed in some detail.

The range of thermocouples of type S or R is limited by the melting point of platinum, 1769 °C [2,3], while the temperature of the 30–6 thermocouple must be kept below the liquidus of the platinum-rhodium 6 percent element, about 1820 °C [4]. The actual upper useful limits are below the temperatures mentioned, especially for the thermocouple of the two alloys where the uncertainty in the liquidus of the 6 percent alloy may be as great as 20 °C. It probably is safe to say, however, that the upper usable limit is extended by at least 30 °C through the use of the all-alloy thermocouple. As an indication of the upper limit of the rhodium 40 percent versus rhodium 20 percent alloy, Acken [4] shows the liquidus of platinum-rhodium 20 percent to be about 1850 °C±20 °C.

Another decided advantage of the 30–6 thermocouple that may be more important than those mentioned above is the very small emf in the normal reference temperature range, from 0 °C to 50 or 100 °C. The emf of this thermocouple is only about 7 microvolts (μv) at 25 °C [5] when the reference junction is at 0 °C, and increases to 56 μv at 100 °C. Errors arising from uncertainties in or ignoring the temperature of the reference junction are therefore relatively small for measurements at high temperatures. The errors for several reference and measuring junction temperatures are given in table 1.

The negative sign of the table points out that values taken from the calibration are too low, and that corrections to temperatures corresponding to the observed emf must be positive. The error is seen to be about 5 °C at a reference temperature of 100 °C and measured temperatures of 1200 to 1800 °C. The errors are greater at the lower measured temperatures; but when it is remembered that this thermocouple is intended for use in the upper range and the reference temperature of 100 °C probably is unrealistic for most cases, the temperature of the reference junction may be ignored

TABLE 1. *Errors due to assuming the temperature of the reference junction of a* Pt-Rh *30 percent versus* Pt-Rh *6 percent thermocouple to be at 0 °C when it is at some higher temperature*

Actual temperature of reference junction	Errors, degrees C at measuring junction temperatures of							
	600	700	800	1,000	1,200	1,400	1,600	1,800
°C								
20	−0.8	−0.7	−0.7	−0.5	−0.5	−0.4	−0.4	−0.4
40	−2.4	−2.0	−1.9	−1.5	−1.3	−1.2	−1.2	−1.2
60	−4.4	−3.7	−3.4	−2.8	−2.5	−2.3	−2.3	−2.3
80	−6.7	−5.6	−5.3	−4.3	−3.8	−3.6	−3.5	−3.5
100	−9.4	−8.0	−7.4	−6.1	−5.3	−5.0	−5.0	−5.0

in general use. This idea is substantiated by the smaller errors at lower reference and higher measured temperatures.

If the temperature of the reference junction is measured, the corrections can be applied to the temperatures corresponding to the measured thermal emf. Linear interpolation between reference temperatures of table 1 causes no further errors, and when applied to measured temperatures leads to an added error of only 0.3° at 750 °C when the reference temperature is 100 °C. The errors introduced by linear interpolation become smaller at higher measured temperatures, and thus are insignificant. If the highest accuracy is desired, the use of an ice bath [6] to keep the reference junction at 0 °C is indicated.

Errors for a type S thermocouple under similar conditions are presented for comparison in table 2.

TABLE 2. *Errors due to assuming the temperature of the reference junction of a* Pt-Rh *10 percent versus* Pt *thermocouple to be at 0 °C when it is at some higher temperature*

Actual temperature of reference junction	Errors, degrees C at measuring junction temperatures of		
	800	1,200	1,600
°C			
20	−10.4	−9.4	−9.5
60	−33.4	−30.3	−30.7
100	−60.1	−53.6	−54.3

Here the value at a reference temperature of 20 °C and a measured 1600 °C is −9.5 °C or about 24 times that for the 30–6. At temperatures of 100° and 800 °C the error is −60.0 °C, and the ratio of errors therefore is about 8. The advantage, consequently, from the standpoint of the small effect of the temperature of the reference junction of the all-alloy thermocouple is obvious. Errors for the type R thermocouple are smaller than those presented in table 2 by about 12½ to 14 percent because of the greater thermal emf of the type R thermocouple in the upper temperature range.

Reference tables for the platinum −10 and −13 percent rhodium versus platinum thermocouples are given in the National Bureau of Standards Reference Tables [7]. No NBS reference table is yet available for the platinum −30 percent rhodium versus platinum −6 percent rhodium thermocouple, but a table published for this com-

bination is presented in table 1 of the appendix.

Of the three thermocouples under discussion, type R provides the greatest thermoelectric output and thermoelectric power, type S the next, and the 30–6 the smallest. A comparison of the three, from the references just cited, is given for 600 °C and above in table 3.

TABLE 3. *Thermal emf and thermoelectric power of type R, type S, and* Pt-Rh *30 percent versus* Pt-Rh *6 percent (30–6) thermocouples*

Type	Emf and thermoelectric power, reference junction at 0 °C, for temperatures, °C, of							
	600		800		1,200		1.600	
	mv	*μv/°C*	*mv*	*μv/°C*	*mv*	*μv/°C*	*mv*	*μv/°C*
R	5.563	11.35	7.924	12.30	13.93	13.85	18.727	13.70
S	5.224	10.20	7.329	10.90	11.935	12.00	16.716	11.85
30–6	1.796	5.95	3.162	7.55	6.811	10.50	11.260	11.30

The thermal emf of the 30–6 combination ranges from 34 percent of the type S and 32 percent of the type R, at 600 °C, to 67 and 60 percent at 1,600 °C. The ranges of thermoelectric power for the same temperatures are from 58 and 52 percent to 95 and 82 percent. Thus it is seen that over the range considered here no great loss of precision will be introduced through the use of the 30–6 thermocouple, and that any such loss may be outweighed in ordinary use by the advantages of this thermocouple.

A disadvantage of the smaller emf of this thermocouple, especially in the lower range, is that the noise of a control system containing electronic components becomes a larger fraction of the total signal as the thermocouple emf decreases. The accuracy of a measuring system that includes a low-emf thermocouple will be lowered unless some way is employed to eliminate or compensate for the noise. Another feature that is related directly to the low emf in the reference temperature region is the small thermoelectric power at 500 °C and below. The change in emf per degree C is about 5μv at 500 °C and drops to less than 0.5 μv per degree at 25 °C.

This thermocouple cannot be used even with an ice bath for high accuracy in this region, and if high accuracy is required in both the lower and upper ranges, the type R or S thermocouple should be used with an ice bath. None of these thermocouples is intended primarily for use in the lower range, though, and unless some experimental factor requires the use of one thermocouple from the lowest to the upper range, a more suitable thermocouple should be used in the lower range.

The limits of error for types R and S thermocouples are given by suppliers normally as 3 °C (5 °F) in the lower range, and to ⅜ percent or ½ percent of the measured temperature in the upper range. In one case, and possibly more, the limits are given as 1.4 °C (2.5 °F) and ±0.25 percent for the lower and upper ranges. Limits as stated in catalogs generally express the degree of agreement with the tables of NBS Circular 561. The ranges are not uniform among suppliers; the lower range as quoted varies from −18 °C (0 °F) or 0 °C (32 °F) to from 538 °C (1,000 °F) to 721 °C (1,330 °F). The upper limit cited extends from 1,316 °C (2,400 °F) to 1,482 °C (2,700 °F). The limits of error given in reference 1 for platinum-rhodium versus platinum thermocouples are ±5 °F (2.8 °C) from 32 to 1,000 °F (0 to 538 °C) and ±0.5 percent from 1,000 to 2,700 °F (538 to 1,482 °C). These thermocouples can be used at temperatures above the maximum limits given, with possible shortening of their useful life.

Accuracy of calibrations made at the National Bureau of Standards of types R and S thermocouples as described in reference [8] follows. The first statement is for calibrations against an NBS standard platinum-rhodium 10 percent versus platinum thermocouple.

"The certified accuracy of calibration of platinum versus platinum-rhodium thermocouples is 0.5 degrees C (0.9 °F) in the range 0 to 1,100 °C (32 to 2,012 °F), and ranges from 0.5 degree at 1,100 °C to 2 (3.6 °F) degrees at 1,450 °C (2,642 °F). Results above 1,100 °C are obtained by extrapolation."

For the primary calibration at four fixed points the accuracy is given as : ". . . the certified accuracy of calibration is 0.3° (0.5 °F) from 0 to 1,100 °C and ranges from 0.3° at 1,100° to 2° (3.6 °F) at 1,450 °C (2,642 °F). Accuracy of certification at the fixed points is 2 μv. If the submitted thermocouple meets the International Temperature Scale requirements for standard thermocouples (see the International Temperature Scale of 1948 by H. F. Stimson, J. Research NBS **42**, 209, 1949), a quadratic equation fitted at the freezing points of antimony, silver, and gold will also be furnished." Specifications for thermocouples submitted for either type of calibration will be found in reference [8].

In the laboratory a thermocouple may conveniently be connected to a measuring instrument using copper leads which join the thermocouple wires in an ice bath. This is normally not practicable in industrial applications where the instrument is remote from the sensing part of the system, since it would require either considerable amounts of prohibitively expensive wire or locating an ice bath near the thermocouple. Lead, or extension, wires of base metals and alloys are available which have the same temperature-emf relationship around ambient temperature as the rare-metal thermocouple for which they were designed as leads. For base metals, smaller wires of the same nominal composition as the thermocouple elements very often are used as extension leads.

Proper use of such leads makes it possible and practical, in effect, to extend the thermocouple to the measuring instrument which customarily in industrial applications contains automatic compensation for the cold junction. Leads for the

types R and S thermocouples have copper as the positive element and a copper-nickel alloy as the negative wire. Generally the range for these leads is stated as 24 to 204 °C (75 to 400 °F) and the limit of error resulting from the use of the leads for regular-grade wires is given as ±7 °C (13 °F). In one instance and possibly others, limits of error for the regular-grade leads are given as ±6 percent or ±5 °C (9 °F) for both types R and S, and the limits for premium-grade extension wires are given as ±2½ percent for type R and 1½ percent for type S. Limits given as percentages apply to the difference between the temperature at the connection to the thermocouple and the temperature at the measuring instrument. Where the error derived from the percent value is smaller than that given in degrees, it is considered to be the limit, rather than the quantity given in degrees.

A word of caution may be worthwhile here on the use of extension leads. Although the lead wires have, within limits, the same temperature-emf relationships as the rare-metal thermocouples, the positive copper and platinum-rhodium are not thermoelectrically neutral, nor are the negative copper-nickel alloy and platinum. These facts lead to the requirement that the temperature of the two leads be the same at any junction with any other material, as for example, at the connection to the thermocouple or to switches. If this condition is not fulfilled, large errors may result.

The possibility of large errors normally is not present in thermocouples mounted by suppliers or manufacturers in tubes with heads in which connectors are mounted. The chief danger lies in the use of unmounted wires where the junctions may be separated and subjected to different conditions of drafts, radiation, etc.

Physical and chemical properties of thermocouple elements of the platinum metals have been assembled from several sources, one of the most fertile of which is the excellent work of Vines [9]. Many of the references cited here have been taken directly from his book, and are so credited. Another excellent source of information on metals in general is the Metals Handbook, American Society for Metals, 1948 edition [10]. The properties given for the platinum metals in this section and for platinum and other metals later are those that may influence the utility of a thermocouple and the accuracy of results obtainable with it.

One of the more important properties of good thermocouple wires is the uniformity of composition and physical condition throughout. Errors will arise when a region of chemical or physical inhomogeneity of a thermocouple is in a temperature gradient. This is so, not only for the rare-metal thermocouples discussed in this section, but also for any thermocouple used for measurement of temperature. Among those who have presented discussions on the subject of homogeneity are Roeser and Lonberger [6], McElroy [11], and Potts and McElroy [77]. In addition, references [11] and [77] give quantitative information on effects of inhomogeneities and equipment for testing for homogeneity. These reports involve chiefly the nickel-base elements exclusive of those with copper, but the treatment is applicable to any thermocouple wires. The chief point that is made, however, is the real importance of homogeneity.

Platinum and the alloys considered here are available in a wide range of wire diameters from, within reasonable limits, as large as desired down to a fraction of a mil (0.001 in.). The most popular diameter, from the standpoint of economy and convenience of handling, seems to be about 20 mils or 0.5 mm. The larger wires are used where greater strength and rigidity are wanted, and where fast response to temperature changes and effects of conduction and radiation are relatively unimportant. Smaller wires are used where one or more of these items becomes important.

As are the other platinum metals, platinum is resistant to corrosion by the common acids and chemicals. It is unaffected by any single acid, but is dissolved by aqua regia. The platinum-rhodium alloys are equally resistant and are said to be unaffected by aqua regia when they contain more than about 20 percent rhodium. These thermocouples should be used under oxidizing or neutral conditions. Platinum and its alloys with rhodium deteriorate under reducing conditions at high temperatures by absorbing gases and metals reduced from the oxides of insulating refractories in contact with them. Commonly used refractories are sources of silicon contamination under adverse conditions. Among the more common reducing atmospheres encountered in practice are those containing carbon and sulfur. Exposure of the platinum versus platinum-rhodium thermocouples to these conditions at high temperature must therefore be avoided. The effect of silicon in a reducing atmosphere was pointed out by McQuillan [12], who found that platinum in the presence of silicon failed in less than an hour. No effect was observed though, in the presence of alumina, beryllia, or carbon in 6½ hr.

A more complete statement on the resistance of platinum to specific agents is found in reference [10], page 1,122, the material of which is credited to the Corrosion Handbook [13]. F. E. Carter [10] gives the resistance to corrosion of the platinum-rhodium alloys as ". . . as good as or better than that of pure platinum at ordinary temperatures, and at high temperatures is usually better than the resistance of pure platinum, except under sulfidizing conditions."

In unpublished work by Olsen at the National Bureau of Standards, platinum has been found to be an active catalyst in dilute mixtures of hydrogen in air, and carbon monoxide in air, to the extent that temperature measurements in such mixtures are subject to large errors. Products of incomplete combustion in, for example, burners

using hydrocarbon fuels thus may be responsible for the same effects which appear at temperatures as low as about 120 °C. Although no quantitative corrections can be given for thermocouples exposed to residual combustibles and oxidant, caution should be exercised in interpretation of data obtained under such conditions with platinum versus platinum-rhodium thermocouples.

Annealed platinum is so soft that is cannot be used bare in high-velocity streams of hot gases or as a long cantilever in quiescent hot gas or vacuum without bending. Some means of protection must be used in such cases, but this often imposes other disadvantages, such as slower response to changes, increased losses due to conduction, etc. The all-alloy thermocouple described earlier has some advantage in this respect because of the increased stiffness of the alloy wires over that of the platinum.

Complete annealing of very pure platinum is said by Vines [9] to occur at 400 °C (752 °F). The time required for this treatment is not specified, but Wise and Vines [14] have stated the temperatures required for complete annealing of 99.9+ percent pure platinum after exposure for 15 min. Their statement is: "The temperatures required to produce complete softening of this platinum in a 15-minute anneal are approximately 765, 700, 635, 600, 545, and 425 °C respectively for reductions in thickness of 19, 39.5, 50.8, 66, 80.5, and 89.5%." Here it is seen that as the percentage reduction of area, or cold working, is increased, the temperature for complete softening is decreased; and that after severe reduction by drawing of extremely pure platinum of thermocouple grade, annealing at 500 °C (932 °F) for 15 min probably would be more than sufficient. At the National Bureau of Standards, however, the regular procedure is to anneal electrically for one hour at 1,450 °C (2,642 °F). This does not produce appreciable adverse effects in the strength of the wire, and may oxidize or otherwise minimize effects of impurities in the wires.

Although the user of thermocouples of platinum and its alloys with rhodium normally is not concerned with numerical data on their mechanical properties, certain properties are related to mechanical behavior and will be given. The annealed condition is the only one of interest for thermocouples, but some information on the cold-worked state is presented for comparison. Grades of platinum discussed are according to the designations of table 1 of Vines [9], which follow in table 4.

TABLE 4.—*Grades of platinum*

Grade	Minimum platinum content	Refiners' designations
	%	
1	99.99	Thermo-element, physically pure or chemically pure.
2	99.9	Chemically pure, special pure, or specially refined.

These grades are equivalent to types A and B of Carter [15].

The tensile strength of grade 1 annealed platinum has been given by Sivil [16] as about 18,000 psi. Wise and Eash [17] found that the tensile strength of grade 2 platinum increased from 22,000 psi in the annealed condition to 36,000 psi after a reduction in area of 50 percent by cold-drawing. In later work an increase was found from 19,350 psi to 29,500 psi after cold-swaging 50 percent. The above values obtained at room temperature.

Wise and Eash [17] reported a tensile strength at room temperature, after annealing at 1,200 °C (2,192 °F), for an alloy of 90 percent platinum and 10 percent rhodium, of 47,000 psi. After 50 percent reduction by cold working the tensile strength was 84,300 psi.

The reduction in tensile strength on heating of platinum and platinum-rhodium 10 percent, annealed at 1,100 °C (2,012 °F), is seen in the following values taken from Wise and Eash [18].

TABLE 5. *Tensile strengths of platinum and platinum-rhodium 10 percent at room temperature and at 1,000 °C (1,832 °F)*

Composition	Tensile strength	
	Room temperature	1,000 °C
	psi	*psi*
Grade 2 platinum	20,700	4,080
Pt-Rh 10 percent	47,900	13,600

The variation of tensile strength with temperature for the platinum-rhodium 10 percent alloy is given in table 6 from Carter and Stauss [19].

TABLE 6. *Tensile strength of platinum-rhodium 10 percent at elevated temperatures*

Temperature		Tensile strength, psi. Wire diameter, in.	
		0.050	0.010 0.003
°C	°F		
20	68	45,000	45,000
500	932	29,700	31,950
700	1,292	24,300	25,650
900	1,652	17,100	19,350
1,100	2,012	10,350	13,050
1,300	2,372	----------	6,750
1,500	2,732	----------	3,600

The above values have been derived from the ratio of tensile strength to that at 20 °C given by Vines from Carter and Stauss.

Vines also gives the values of tensile strength as determined by Carter and Stauss for several alloys of platinum and rhodium which cover the thermocouple compositions up to 20 percent rhodium. This information, in table 7, is for a temperature of 20 °C.

Small amounts of alloying impurities have an appreciable effect on the tensile strength of platinum, according to Vines [9], and their effect is even more pronounced on the proportional limit. This is shown along with the proportional limit for platinum-rhodium 10 percent in table 8 taken from table 14 of reference [9].

TABLE 7. *Tensile strengths of several platinum-rhodium alloys at 20 °C (68 °F)*

Rhodium	Ultimate tensile strength	
	Hard	Annealed
%	*psi*	*psi*
0	34,000	18,000
3.5	60,000	25,000
5	70,000	30,000
10	90,000	45,000
20	130,000	70,000

TABLE 8. *Proportional limits of platinum and platinum-rhodium 10 percent*

Alloy	Proportional limit, cold worked, 50 percent reduction	Annealing temperature	Proportional limit annealed
	psi	°C	*psi*
Grade 1 platinum		900	<2,000
Grade 2 platinum	27,000	1,000	2,000–5,500
Platinum-rhodium 10 percent	55,600	1,200	17,000

Most of the more commonly considered physical properties of the platinum and platinum-rhodium thermocouple elements have direct bearings upon their performance in temperature measurements; some, in addition, are of value in selecting wires of high purity and for special uses.

The purity of platinum often is inferred from two electrical quantities, the thermal emf and $\alpha=(R_{100}-R_0)/(100R_0)$, where R is resistance and the subscripts refer to degrees C. Because all known impurities likely to be found in platinum, with the exception of gold in detectable quantity, make the thermal emf positive, the more negative a sample of wire is in this respect, the purer it is considered to be. A sample of extremely pure platinum made at NBS in 1922 and known as Pt 27 has been kept as a reference, and has served as a standard against which much of the platinum used in thermocouples has been compared. In the early days of Pt 27 practically all platinum was thermoelectrically positive to it, but recently high grade platinum neutral to Pt 27 has become fairly common, and some samples as much as 8 or 10 μv negative have appeared.

The α mentioned above probably is a more reliable indication of purity of platinum than is the thermal emf; and can, for very pure platinum, be correlated with thermal emf. Since any impurities reduce the value of α, the correlation is between ascending α and more negative thermal emf. It appears at present that the ultimate value of α for platinum with no impurities present is in the neighborhood of 0.003928, a value which has been obtained for a few samples. Platinum with an α of 0.003923 is available commercially and values up to 0.003927 are attainable if sufficient care in refining and handling is exercised. It thus appears that a material standard such as Pt 27 has outlived its usefulness, and that reference samples kept for comparison might be described in terms of the relationships between thermal emf and α of the samples.

Data on the resistivity of 0 °C and relative resistivity of platinum and the conventional platinum-rhodium thermocouples taken from Roeser and Wensel's [20] table are presented in table 9. Resistivity is given here in ohms per circular mil foot (ohms/cmf), and the ratios in some cases have been adjusted slightly to convert to degrees C 1948 Int.

TABLE 9. *Relative electrical resistivities at temperatures to 1,500 °C of platinum,* Pt-Rh *10 percent, and* Pt-Rh *13 percent*

	Platinum	Pt-Rh 10 Percent	Pt-Rh 13 Percent
Resistivity at 0 °C, ohms/cmf	59.1	110.7	114.3
Temperature °C	R_t/R_0	R_t/R_0	R_t/R_0
0	1.000	1.000	1.000
20	[a] 1.056	[b] 1.030	[c] 1.03
100	1.392	1.166	1.156
200	1.773	1.330	1.308
300	2.142	1.490	1.456
400	2.499	1.646	1.601
500	2.844	1.798	1.744
600	3.178	1.947	1.885
700	3.500	2.093	2.023
800	3.809	2.233	2.156
900	4.108	2.369	2.286
1,000	4.395	2.503	2.414
1,100	4.672	2.633	2.538
1,200	4.933	2.760	2.659
1,300	5.184	2.883	2.779
1,400	5.423	3.009	2.896
1,500	5.650	3.130	3.011

[a] Calculated from R_0 and equation of reference [9], page 20.
[b] From reference [9], table 42.
[c] From figure 3 of reference [21].

An equation relating the resistivity of platinum at temperatures up to 1,500 °C, and giving values near those of Roeser and Wensel is:

$$R_t=R_0(1 + 3.9788 \times 10^{-3}\, t - 5.88 \times 10^{-7}\, t^2)$$

The electrical resistivities at 20 °C of four platinum-rhodium alloys are given in table 10 [22].

TABLE 10. *Electrical resistivity at 20 °C of four* Pt-Rh *alloys*

Percent rhodium	Resistivity at 20 °C
	ohms/cmf
3.5	99.9
5	105.3
10	115.5
20	125.1

The density of annealed platinum at 20 °C appears to be generally accepted as 21.45 g/cm³. The densities of some platinum-rhodium alloys as given by Carter [22] are presented in table 11.

TABLE 11. *Density at 20 °C of some platinum-rhodium alloys*

Weight percent rhodium	0	3.5	5	10	20	30 [a]	100 [b]
Density, g/cm³	21.45	20.9	20.65	19.97	18.74	17.6	12.414
Density, lb/in.³	0.7749	0.755	0.746	0.721	0.677	0.636	0.448

[a] From reference [4], figure 3, density at 25 °C, sample annealed at 1,500 °C.
[b] As given by Vines [9], attributed to Holzmann (1931).

TABLE 12. *Thermal expansion of platinum,* Pt-Rh *20 percent, and rhodium relative to length at 0 °C* (l_t/l_0)

Temperature	(l_t/l_0)		
	Platinum	Pt-Rh 20 percent	Rhodium percent
°C			
0	1.000000	1.00000	1.00000
20	1.000180	1.00018	1.00016
25	1.000225	1.00022	1.00020
50	1.000452	1.00044	1.00040
75	1.000680	1.00067	1.00062
100	1.000909	1.00089	1.00085
200	1.001841	1.00182	1.00180
300	1.002796	1.00278	1.00280
400	1.003773	1.00377	1.00385
500	1.004776	[a] 1.00480	1.00490
600	1.005803	1.00586	1.00600
700	1.006853	1.00695	1.00710
800	1.007931	1.00807	1.00825
900	1.009039	1.00922	1.00949
1,000	1.010176	[a] 1.0104	1.01080
1,100	----------	1.0116	1.0121
1,200	----------	1.0128	1.0135
1,300	----------	1.0141	----------
1,400	----------	[a] 1.0154	----------
1,500	----------	1.0167	----------

[a] These points are given in reference [24].

The thermal expansions of platinum [23], platinum-rhodium 20 percent [24], and rhodium [9] are presented in table 12.

Very few data seem to be available on the alloys, and rhodium is included in table 12 as a guide for approximate estimation. Only three values were available for the alloy of 20 percent rhodium, and so the others were obtained by interpolation with a cubic equation. Slight adjustments were made in a few cases to place the data on the 1948 temperature scale. The equation given by Esser and Eusterbrock in reference [23] for the thermal expansion of platinum is:

$$l_t=l_0(1+8.9877\times10^{-6}t+0.0010652\times10^{-6}t^2 +0.0000001256\times10^{-6}t^3)$$

Jaeger and Rosenbohm [25] have given equations for the heat content of platinum at temperatures from 0 to 1,600 °C and values of mean specific heat ($\overline{C}_p$) from 20 to 400 °C. An equation is given for $\overline{C}_p$ from 20° to temperatures in the range 400 to 1,600 °C. The data are said by the authors to be good to ±0.1 percent. The equations for the heat content are:

for temperatures between 0 and 500 °C

$$Q_{(t°-0°)}=0.031357t+0.04507\times10^{-4}t^2-0.0161\times10^{-7}t^3, \quad \text{I (A)}$$

and for temperatures between 400 and 1,600°

$$Q_{(t°-0°)}=0.031622t+0.03172\times10^{-4}t^2. \quad \text{I (B)}$$

Values of specific heat for platinum in table 14 have been obtained by differentiating and substitution of temperatures in the above equations. In the region of overlap, 400 to 500 °C, agreement between data obtained is not so good, and a slight discontinuity is seen in the region where the two equations join. Values at 400 °C and below were obtained from equation I(A) and those above are from I(B).

Mean specific heats above 20 °C are tabulated up to 400 °C and an equation is given for higher temperatures. The tabulated values are given in table 13, and the equation for the mean specific heat, $\overline{C}_{p(t°-20°)}$, follows. From 400 to 1,600 °C $\overline{C}_{p(t°-20°)}=0.031701+0.03164\times10^{-4}t$.

TABLE 13. *Mean specific heat above 20 °C of platinum*

Temperature	$\overline{C}_{p(t°-20°)}$ cal/g °C
°C	
100	0.03187
200	.03228
300	.03264
400	.03296

Other values of specific heat of platinum are found in Vines [9] and the 1948 edition of the Metals Handbook.

No determinations of the specific heats of platinum-rhodium alloys seem to be available. The values of Jaeger and Rosenbohm [25] for rhodium up to 1,300 °C are presented in table 14.

TABLE 14. *True specific heats of platinum and rhodium*

Temperature	Specific heat, cal/g °C		Temperature	Specific heat, cal/g °C	
	Platinum	Rhodium		Platinum	Rhodium
°C			°C		
0	0.03136	0.05893	800	0.30670	0.07618
25	.03158	.05922	900	.03733	.07814
50	.03180	.05953	1,000	.03797	.07969
100	.03221	.06026	1,100	.03860	.08074
200	.03297	.06203	1,200	.03924	.08119
300	.03363	.06415	1,300	.03987	.08092
400	.03419	.06650	1,400	.04050	----------
500	.03466	.06899	1,500	.04114	----------
600	.03543	.07150	1,600	.04177	----------
700	.03606	.07393			

The equation from which these values were calculated is that given by Jaeger and Rosenbohm:

$$C_p=0.05893+1.066\times10^{-5}\ t+2.7744\times10^{-8}\ t^2 -1.7642\times10^{-11}\ t^3.$$

Further values of the specific heat of rhodium may be found in reference [9], and numerous values of thermal properties of platinum and some other metals are included in reference [26], which, together with reference [27], is a prolific source of thermal properties of some metals.

TABLE 15. *Thermal conductivity of platinum*

Temperature	Thermal conductivity	Temperature	Thermal conductivity
°C	cal/sec/cm²/cm/°C	°C	cal/sec/cm²/cm/°C
0	0.1660	600	0.1943
20	.1669	700	.1991
100	.1707	800	.2038
200	.1754	900	.2085
300	.1802	1,000	.2132
400	.1849	1,100	.2180
500	.1896		

Almost all of the information on thermal conductivity of platinum is for the low range, from room temperature to 100 °C, and no data seem to be available for the platinum-rhodium alloys in the higher range. Values calculated from the equation of Holm and Störmer [28] are given in table 15, and their equation follows. The equation used to calculate the values of table 15 is

$$k=0.699[1+2.83\times 10^{-4}\ (t-19.5)].$$

In this case the thermal conductivity, k, is in watts/cm²/cm/°C. Values obtained from the equation were multiplied by 0.2388 to convert to the units given in the table.

Only one value of thermal conductivity for platinum-rhodium alloys has been found. This, for platinum-rhodium 10 percent (reference [3], p. 138), is 0.072 cal/sec/cm²/cm/°C at a temperature of 18 °C. Alpha (α) in the equation $k_t=k_0[1+\alpha(t-t_0)]$ is given as +0.0002, where k_0 is the conductivity at 18 °C and t refers to some other temperature. No reference to the original paper is given in reference [3], so that the limitations of this equation are unknown.

A considerable amount of information is found on the emissivity (ϵ) of platinum. Some disagreements are seen between the various investigators, and the tables that follow are given either because they provide the most recent data, or are the only sources found. No information on the platinum-rhodium alloys seems to be available.

The total emissivity of platinum as given by Geiss [29] follows in table 16. Note that temperature in this table and some of the following are in °K and not °C.

TABLE 16. *Total emissivity, ϵ, of platinum*

Temperature	ϵ	Temperature	ϵ
°K	*percent*	°K	*percent*
500	7.31	1,100	13.4
600	8.41	1,200	14.3
700	9.48	1,300	15.2
800	10.5	1,400	16.1
900	11.5	1,500	17.0
1.000	12.75	1,600	17.8

Emissivity, in this paper, refers to the ratio of energy radiated hemispherically per unit area per unit time by a surface to that radiated by a blackbody at the same temperature.

Spectral emissivities of platinum of Worthing [30] are given in table 17.

TABLE 17. *Spectral emissivities of platinum at wavelengths (microns) of*

Temperature	0.665 μ	0.535 μ	0.460 μ
°K			
1,200	0.295	0.325	0.375
1,600	----------	0.335	----------
1,850	0.310	----------	0.390

Values of table 18 by Stephens [31] are for the emissivity of platinum at 0.660μ, in the wavelength region most commonly used in optical pyrometry. Brightness temperatures corresponding to true temperatures are included.

TABLE 18. *Emissivity and brightness temperature of platinum at 0.660 μ*

True temperature	$\epsilon_{0.660\ \mu}$	Brightness temperature	True temperature	$\epsilon_{0.660\ \mu}$	Brightness temperature
°K		°K	°K		°K
1,200	0.283	1,121.6	1,600	0.291	1,466.5
1,250	.284	1,165.4	1,650	.292	1,508.8
1,300	.285	1,209.0	1,700	.293	1,550.8
1,350	.286	1,252.5	1,750	.294	1,592.7
1,400	.287	1,295.6	1,800	.295	1,634.4
1,450	.288	1,338.6	1,850	.296	1,676.0
1,500	.289	1,381.4	1,900	.297	1,717.4
1,550	.290	1,424.1			

Emissivities of platinum in the infrared as determined at 1,125 °C by Price [32] are presented in table 19.

TABLE 19. *Spectral emissivity of platinum in the infrared at 1,125 °C*

μ	ϵ	μ	ϵ
	percent		*percent*
0.65	22.0	2.5	21.8
1.0	29.3	2.75	20.6
1.1	28.7	3.0	19.6
1.2	28.4	3.25	18.8
1.3	28.4	3.5	18.0
1.4	27.6	3.75	17.2
1.5	27.0	4.0	16.5
1.75	25.5	4.25	15.7
2.0	24.0	4.5	15.0
2.25	22.8	4.75	14.5

The first value of table 19, 22.0 percent at 0.65 μ, was suspect, and on referring to the original paper was found to be as published. On further examination, however, it was found that this value apparently should be 33.0, which still seems to be too great a change in the opposite direction.

Neither platinum nor its alloys is magnetic at room temperature.

The volatility of platinum is indicated, according to the work of Jones, Langmuir and MacKay [33], by the data given in table 20, taken from reference [9].

TABLE 20. *Volatilization of platinum in vacuo*

Temperature, °C	527	727	1227	1727
Loss, g/cm²/sec	1.39×10^{-26}	6.7×10^{-20}	5.23×10^{-11}	1.24×10^{-6}

According to Crookes [34] platinum is twice as volatile as rhodium in air at 1,300 °C, one-third as volatile as palladium, and one-thirtieth as volatile as iridium. According to Vinès, "It should be emphasized . . . that this order of volatility applies to tests in air where the oxidation of some of these metals and volatilization of the oxides is a factor . . ."

b. Iridium Versus Iridium-Rhodium Alloys

Feussner [35] proposed in 1933 the use of thermocouples of iridium-rhodium alloys versus iridium "for very high temperatures." Several alloys have been proposed for the positive wire of the thermocouple, chief among these being alloys of 40, 50, and 60 percent iridium with rhodium. Various reasons have been given for the choice of a particular one of these compositions. The thermal emfs of the 40 and 60 percent wires are not widely different, and are not too far below the maximum, which occurs at about the 50-50 composition. One point made by some is that loss of iridium from the 60 percent wire will alter the thermal emf toward its maximum and not toward the steeper slope in the other direction, and that the temperature range of the alloy containing more iridium will be somewhat greater. The latter point is well taken, and because of this the 60 percent alloy is enjoying greater popularity as time passes. The alloy of 40 percent iridium-60 percent rhodium has been used in the past, however, and probably will continue to be used for some time.

A considerable amount of work has been done on the properties of iridium, but information on the alloys of iridium and rhodium is very scarce, almost to the point of nonexistence. The little data that are available are given, however, and some calculated data that should be used with caution are added.

The temperature limit of use of the iridium-rhodium versus iridium thermocouples is set by the liquidus-solidus temperature of the alloy wire, and not, as in the case of the platinum-rhodium versus platinum thermocouples, by the freezing point of the pure wire. The freezing point of iridium is given by Henning and Wensel [36] as 2,454 ±3 °C on the International Temperature Scale of 1927. This becomes 2,443° on the 1948 scale. No liquidus-solidus temperatures are found for the iridium-rhodium system, but approximate values may be inferred from the freezing points of iridium and rhodium [37]. If the assumption is made that the liquidus-solidus curve for the iridium-rhodium system is similar to Acken's [4] for the platinum-rhodium system, then values obtained by linear interpolation from iridium to rhodium would be on the safe side. Justification for this is tenuous, but some values are given in table 21.

One approximate check has been made in Blackburn and Caldwell's work [38] on the validity of a value for the 60 percent rhodium-40 percent iridium alloy. On heating a thermocouple having this alloy as one wire until it broke, the limiting temperature was found to be below 3,900 °F. The calculated temperature from table 21, 2,157 °C, is 3,915 °F. The upper safe limit for calibration of this thermocouple accordingly was set at 3,800 °F (2,093 °C). Judging from this case, it will be necessary, in order to provide a safe margin, to keep the temperatures of the other two

TABLE 21. *Calculated liquidus-solidus temperatures for three iridium-rhodium alloys*

Composition	Liquidus-solidus temperature
%	°C
100 Rh	[a] 1960
60 Rh 40 Ir	2,153
50 Rh 50 Ir	2,202
40 Rh 60 Ir	2,250
100 Ir	2,443

[a] The value of the freezing point of rhodium has been adjusted to put it on the 1948 Temperature Scale.

alloys at least 60 °C (108 °F) below the values of table 21. These limits were arrived at solely on the basis of temperatures at which the wires soften or melt; other properties that limit the use or life of such thermocouples are discussed later.

Several determinations have been made of the temperature-emf relationships of iridium 40 percent-rhodium 60 percent versus iridium thermocouples. Among these are the work of Droms and Dahl [39] of the General Engineering Laboratories of the General Electric Company, and of Blackburn and Caldwell at the National Bureau of Standards. A report on the latter work, containing reference tables, is included in this symposium [38]. From results of the investigation of this alloy, and from preliminary observations on alloys containing 60 percent iridium and 50 percent iridium, it appears that the 50–50 alloy will be the optimum, even at the expense of a slight lowering of the upper range of use under that of the alloy containing 60 percent iridium.

A condensed version of Blackburn's reference table for the iridium 40 percent-rhodium 60 percent versus iridium thermocouple is given in table 2A of the appendix.

Table 3A of the appendix gives the emfs of the elements of this thermocouple against copper for use in making corrections for temperatures of reference junctions where connections to the two wires are not at the same temperature.

The thermoelectric power of the iridium-rhodium 40 percent versus iridium thermocouple is seen to be a maximum of about 6 μv/°C (3 μv/°F) in the upper part of the range. In the region of room temperature and somewhat above, the thermoelectric power is about one-half the maximum. The emf is not so low in the lower range though, that, as in the case of the 30–6 thermocouple, the temperature of the reference junction can be ignored without the danger of introducing an appreciable error. Thus junctions of leads of this thermocouple with copper should be in an ice bath, or temperatures of the junctions should be measured and corrected for. Normally the latter course is taken because of the high cost of the alloy and iridium wires.

An estimate of accuracy of the reference table for the thermocouple with the alloy of 40 percent iridium is given by Blackburn. This is for this table only, and does not contemplate errors that

may be involved in the use of this thermocouple. Accuracy is given by one of the suppliers of the iridium 60 percent-rhodium 40 percent versus iridium thermocouple as ±40 °F [40] in the upper part of the range. This is for a thermocouple in packed ceramic insulation, but there seems to be no reason to believe that this type of mounting should affect the accuracy obtainable to any appreciable extent. The accuracy of the thermocouple under discussion may be expected to be about the same. A statement is made in reference [40] also that "Corrections for radiation and conduction cannot be given due to the multiplicity of factors affecting these corrections." This should be borne in mind for this and other thermocouples; such corrections may amount to many times the accuracy stated above.

Calibration data for the iridium 60 percent-rhodium 40 percent versus iridium from reference [122] are included in table 7 of the appendix.

No extension leads are known to be available for the iridium-rhodium versus iridium thermocouples.

No detailed information is available on homogeneity of wires of iridium-rhodium versus iridium thermocouples, but from experience at the National Bureau of Standards it appears that thermal emfs of wires of the same size from the same lot do not vary appreciably. Some small differences are seen though between wires of diameters of 0.035 in. and 0.020 in. that presumably are from the same lot. No work has been done at NBS on wires smaller than 0.020 in. nor larger than 0.035 in.

These thermocouple wires are available in diameters from 0.002 in. up to any reasonable size. The most popular diameter here also seems to be 20 mil, but as in the case of the platinum-rhodium versus platinum thermocouples, experimental conditions may dictate that other sizes be used.

Iridium, according to Vines [9] "is the most corrosion resistant element known; it is unaffected by common acids and is even resistant to aqua regia and fuming sulphuric acid. Small percentages of iridium, up to about 20 percent, also greatly increase the corrosion resistance of platinum and palladium."

The iridium-rhodium versus iridium thermocouples have been used at the National Bureau of Standards in exhausts of afterburners and ramjet burners up to about 50 hrs at temperatures of 3,000 °F. (1,649 °C) and above before failure. The gases were somewhat oxidizing because of incomplete combustion. The thermocouples were mounted for this use in water-cooled mountings, so that only a small portion of the thermocouple was exposed to the hot gases. Failure was caused by loss of the pure wire in the exposed part. Apparently the iridium wire oxidized; and the oxide having, according to Crookes [34], a high vapor pressure, volatilized. No quantative measurements have been made on loss by volatilization from the iridium wire, but on seeing the cloud of black smoke from a length of wire heated electrically above 3,000 °F it is not hard to believe the statement of Crookes [34] that "the loss of iridium in air at 1,300 °C is . . . 30 times that of platinum and 60 times that of rhodium." The alloy wire, from casual examination, did not appear to have lost metal.

A coating ranging from gray to black was seen on the wires on returning from high to room temperatures in the work at the National Bureau of Standards. This coating was thought to be oxide, and subsequent observations were made in an atmosphere of helium that had been passed through a liquid nitrogen trap to remove water vapor and oil. The coating persisted, however, even in helium, and no determination has been made as to the source. It has been established, though, that formation of this coating has no appreciable effect on the thermal emf.

Thus these thermocouples should not be used in strongly oxidizing atmospheres if long life is wanted. They are, however, usable in neutral atmospheres and in vacuo. No statement has been found of effects of reducing atmospheres on these wires or of effects of various refractories. Until information does appear, it seems reasonable to assume for the sake of accuracy and safety that iridium and its alloys with rhodium are affected in a manner similar to platinum.

Iridium is used as a catalyst in some processes, but no definitive work seems to have been done on catalytic effects under conditions of thermocouple use in burners. It seems reasonable to expect that such effects will be present in cases of incomplete combustion, and so care should be taken in interpreting data obtained with iridium-containing thermocouples under such conditions, especially in the lower temperature range.

No procedures for annealing iridium and its rhodium alloys are stated in the literature, but one suggested by Brenner [41] has been adopted at the National Bureau of Standards. In this, a small sample of wire is heated electrically until it melts; the apparent temperature of melting is observed with an optical pyrometer, and the thermocouple wire is annealed for a few minutes at an apparent temperature about 200 °C lower than that observed at melting. Care must be taken in this procedure, especially with the pure wire, because of the effect on the reading of the optical pyrometer of the black smoke generated. Immersion of the hot wires in an atmosphere of inert gas is helpful in preventing oxidation. Helium has been used at the National Bureau of Standards during calibrations.

Care is needed in handling these wires. They are flexible in the annealed state, but cannot stand much cold working such as the bending that occurs in normal use. Wire of 0.035 in. diam has been bent at the National Bureau of Standards into an eye of about 0.25 in. diam. without breaking, but it cannot be straightened again without heating. Several cases have occurred in which the repeated mild bending incidental to changing the reference junction ice bath has broken the wires.

Very little information is available on the mechanical properties of iridium, and none is found on its alloys with rhodium. Perhaps a clue might be had to the tensile strength of iridium from values given in reference [42] for alloys of 5 to 30 percent iridium in platinum. Here the ultimate tensile strength for the hard alloys is seen to increase from 70,000 psi for 5 percent iridium to 200,000 psi for 30 percent iridium. The increase over the same range of compositions for annealed wire is from 40,000 to 160,000 psi. Young's modulus for hard iridium is given as 7.47×10^7 psi.

The thermal emf of iridium versus Pt 27, up to 2,500 °F, from the work of Blackburn [38] is given in condensed form in table 22. The thermal emf of the iridium 40 percent-rhodium 60 percent wire against platinum can be obtained by adding the thermal emf of the iridium 40 percent rhodium 60 percent versus iridium thermocouple to that of iridium versus platinum.

TABLE 22. *Thermal emf of iridium versus Pt 27*

Temperature		Emf	Temperature		Emf
°F	°C	mv	°F	°C	mv
32	0	0	1,300	704.4	7,729
100	37.8	0.227	1,400	760.0	8.596
200	93.3	0.616	1,500	815.6	9.499
300	148.9	1.066	1,600	871.1	10.437
400	204.4	1.565	1,700	926.7	11.410
500	260.0	2.105	1,800	982.2	12.419
600	315.6	2.685	1,900	1,037.8	13.460
700	371.1	3.299	2,000	1,093.3	14.532
800	426.7	3.947	2,100	1,148.9	15,632
900	482.2	4.630	2,200	1,204.4	16.753
1,000	537.8	5.349	2,300	1,260.0	17.893
1,100	593.3	6.106	2,400	1,315.6	19.048
1,200	648.9	6,899	2,500	1,371.1	20.211

The electrical resistivity of iridium is given in reference [42] as 6.08×10^{-6} ohm-cm (36.58 ohms/cmf) at 0 °C. Wilcox and Doring [43] give a value of 31.8 ohms/cmf, which corresponds to the 5.3×10^{-6} ohm-cm at 20 °C attributed by Vines to Jaeger and Diesselhorst [44]. The temperature coefficient of resistance as determined by Holborn [45] is given in table 23. A 1958 value of the temperature coefficient from 0° to 100 °C $\alpha=(R_{100}-R_0)/(100R_0)$ given in reference [43] as 0.0040 per °C indicates that the older value, 0.003925 per °C probably is low.

Values of resistivity of iridium based on resistivities of references [42], [45] are given in table 24. The temperature coefficients of resistance used are those of table 23.

TABLE 23. *Temperature coefficient of electrical resistance of iridium*

Temperature range	Temperature coefficient
°C	per °C
0–100	0.003925
0–200	.00398
0–300	.00404
0–400	.00408
0–500	.00414

TABLE 24. *Electrical resistivity of iridium*

Temperature	Resistivity	
	Reference [42]	Reference [45]
°C	ohms/cmf	ohms/cmf
0	36.6	29.6
20	39.5	31.9
100	51.0	41.2
200	65.6	53.2
300	80.6	65.6
400	96.3	77.6
500	112.	90.8

The two columns of table 24 differ widely, and which is the better is not known. Vines [9] believed the value of reference [45] to be the best, while Carter and Stauss seemed to prefer the newer value at 0 °C of reference [42]. The Smithsonian Physical Tables [3] give 6.1×10^{-6} ohm-cm on page 384 for the resistivity at 0 °C, and also the resistivity at 100 °C as 8.3×10^{-6} ohm-cm, a value that agrees with neither in the table.

The density of iridium from reference [3] is 22.42 g/cm³ (1400 lb/ft³). Vines cites the value of 22.41 g/cm³ of Holborn and co-workers [46], and also points out that the density "calculated from the space lattice, which . . . may be more reliable is 22.65_6 g/cm³ at 0 °C and 22.65_0 at 20 °C according to Owen and Yates [47]". The value given in reference [43] is 22.54 g/cm³. No information is available on the density of the alloys with rhodium; but the value of 12.4 g/cm³ for rhodium at 20 °C, as given in reference [47], may be used to calculate approximate densities of the alloys.

Holborn and Valentiner [48] give the equation

$$l_t=l_0(1+6.6967\times10^{-6}\,t+1.158\times10^{-9}\,t^2),$$

from which the length of iridium at temperatures up to 1,000 °C can be calculated. Values calculated from this equation follow in table 25.

TABLE 25. *Thermal expansion of iridium relative to length at 0 °C* (l_t/l_o)

Temperature	l_t/l_o	Temperature	l_t/l_o
°C		°C	
0	1.000000	600	1.00443
100	1.000681	700	1.00526
200	1.001386	800	1.00610
300	1.002113	900	1.00696
400	1.00286	1,000	1.00785
500	1.00364		

Jaeger and Rosenbohm [49], among others, have determined the specific heat of iridium. Their equation is $c_p=0.030725+7.4004\times10^{-6}t$. Values of true specific heats calculated from this equation are presented in table 26.

The heat content above 0 °C is given by the equation

$$Q_{(t°-0°)}=0.037025\,t+0.0000037002t^2.$$

TABLE 26. *True specific heat of iridium*

Temperature	Specific heat	Temperature	Specific heat
°C	cal/g °C	°C	cal/g °C
0	0.03072	900	0.03742
100	.03147	1,000	.03816
200	.03221	1,100	.03891
300	.03296	1,200	.03965
400	.03370	1,300	.04040
500	.03444	1,400	.04114
600	.03519	1,500	.04189
700	.03593	1,600	.04263
800	.03668	1,700	.04337

The thermal conductivity of iridium has been given by Barratt and Winter [50] as 0.141 cal/sec/cm²/cm/°C at 17 °C and 0.135 at 100 °C.

Information on the emissivity of iridium is scattered. Roeser and Wensel, on page 313 of reference [20], give a value of 0.30 at 0.65μ for the unoxidized solid. Goldwater and Danforth [51] give a value of 0.33 at the same wavelength. Fulk and Reynolds [52] give the total normal emissivity at 295 °K to be 0.04, and a list of normal spectral emissivities at the same temperature. These latter values are given in table 27.

TABLE 27. *Normal spectral emissivities of iridium at 295 °K*

Wavelength	ε	Wavelength	ε
μ	%	μ	%
1.0	22	7.0	5
2.0	13	9.0	4
3.0	9	10.0	4
4.0	6	12.0	4
5.0	6		

Values of the reflectivity of iridium at three wavelengths, from Wise [53], are given in table 28.

TABLE 28. *Reflectivity of iridium*

Percent reflectivity at wavelengths of		
0.450	0.550	0.750μ
64	70	78

Except for the data of Fulk and Reynolds, temperatures at which emissivities and reflectivities are given are not specified. Goldwater and Danforth do say, however, that their value for the emissivity was computed from the relationship between true and brightness temperature at a pyrometer wavelength of 0.65μ.

Both elements of the iridium-rhodium versus iridium thermocouples are nonmagnetic at room temperature.

c. Platinum-Iridium 15 Percent Versus Palladium

This thermocouple having as its elements the positive platinum-iridium 15 percent and the negative palladium wires was developed by the General Electric Company [54] under sponsorship of the Wright Air Development Division of the Air Force. It was developed to provide a sensor that is suitable for extended use at temperatures above the usable range of the more common base-metal thermocouples, and that has a thermoelectric power of the same order as that of the base-metal thermocouples.

The upper range of the platinum-iridium 15 percent versus palladium (PIP) thermocouple is limited by the freezing point of palladium, given as 1,552 °C (2,826 °F) on page 72 of reference [3]. The solidus of the platinum-iridium wire is seen from figure 22 of reference [9] to be about 1,790 °C. This, when corrected to the 1948 temperature scale, is about 1,785 °C, or 3,245 °F. In most cases the upper useful limit of this thermocouple will be found to be somewhat below the freezing point of palladium.

Determinations of the temperature-emf relationship of the PIP thermocouple have been made at the General Electric Company [54] and at the National Bureau of Standards [55]. Tables of reference [55] are similar to those of NBS Circular 561 in which reference tables for the conventional thermocouples are given. A condensed version of these tables for the PIP thermocouple is in table 4A of the appendix. Thermal emfs versus copper of the elements are given in table 5A of the appendix. Thermal emfs of the thermocouple elements versus Pt 27 are presented in table 29.

TABLE 29. *Thermal emf of platinum-iridium 15 percent and palladium versus Pt 27*

Temperature		Platinum-iridium 15 percent	Palladium
°F	°C	mv	mv
32	0	0.000	0.000
200	93	1.309	−0.521
400	204	3.124	−1.224
600	316	5.096	−2.034
800	427	7.168	−3.004
1,000	538	9.296	−4.173
1,200	649	11.475	−5.577
1,400	760	13.692	−7.218
1,600	871	15.950	−9.080
1,800	982	18.258	−11.142
2,000	1,093	20.592	−13.390
2,200	1,204	22.943	−15.787
2,400	1,316	25.262	−18.306
2,550	1,399	26.989	−20.266

Extension leads of alloys of base metals have been developed by the General Electric Company for the PIP thermocouple that provide a reasonable match with the thermocouple up to about 1,300 °F. The calibration has not yet been published, but it is anticipated that it will appear in the near future.

Six thermocouples of platinum-iridium 15 percent versus palladium were used in the determination of the reference tables. Homogenity of the 0.040-in. wires examined is indicated by the maximum divergence of the six thermocouples at 2,500 °F (1,371 °C) of about 3 °F, and much smaller differences at lower temperatures.

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Some of the 0.040-in. wires have been drawn down to 0.010-in. diameter at NBS, and there is no reason to believe that they cannot be reduced to a diameter of a mil or so.

Resistance to corrosion of the platinum-iridium alloy is excellent, and apparently surpasses in this respect the platinum-rhodium alloys discussed earlier. Some loss of iridium is said to occur in the region of 900 °C (1, 652 °F) and above because of formation and volatilization of the oxide. A gray to black film has been seen to form on this wire at about the same temperature when the wire is heated in air. This film may disappear on heating to a temperature two or three hundred degrees higher. Although no detailed information on the resistance of the platinum-iridium alloys to the ordinary products of combustion and reducing conditions is found, as a matter of safety, precautions similar to those described for platinum should be observed.

Palladium is not so resistant to attack by common chemicals as are the other platinum metals discussed previously. According to Vines [9] "Palladium is resistant to corrosion at room temperature by hydrofluoric acid, perchloric acid, phosphoric acid and acetic acid. It is slightly attacked by sulphuric, hydrochloric and hydrobromic acids, especially in the presence of air, and readily attacked by nitric acid, ferric chloride, hypochlorites and moist chlorine, bromine and iodine. In ordinary atmospheres palladium is resistant to tarnish, but some discoloration may occur on exposure to moist industrial atmospheres containing sulphur dioxide." Ihnat [54] points out the following characteristics of palladium:

"1. Palladium is superficially oxidized if heated to a temperature of 700 °C (1,292 °F). The oxide (PdO) formed decomposes above 875 °C (1,607 °F) and a bright metal remains.

2. "Palladium will absorb as much as 800 to 900 times its own volume of hydrogen over a range of temperature.

"3. Subjected to alternate oxidizing and reducing atmospheres surface blistering is apt to result."

The first and third of these have been confirmed approximately in the work on this thermocouple at the National Bureau of Standards.

Both the platinum-iridium and palladium wires are catalytic, and accordingly care should be taken in interpretation of data obtained with them.

Both elements of this thermocouple are readily handled in the annealed state without danger of breaking. Vines' comments on annealing of the wires follow:

"Alloys containing more than 10% iridium require rather high annealing temperatures, in the neighborhood of 1,400 °C to completely soften them in a short time, although in practice, anneals at about 1,100 to 1,200 °C for 30 to 45 minutes are sometimes employed.

"Palladium is very ductile and can be worked hot or cold. As with platinum, it is usual to begin working ingots at about 800 °C to secure more rapid reduction and then finish by cold working. Palladium withstands drastic cold working and, like gold, can be beaten into leaf as thin as 1/250,000 of an inch.

"It is possible that pure palladium can be annealed at a lower temperature than pure platinum but reliable information is not avaliable. Although marked softening occurs at 700 °C, commercial palladium requires an annealing temperature of 800 or 900 °C to obtain maximum ductility with a short anneal. At temperatures outside this range, selective grain growth resulting in lowered ductility may occur in some lots of commercial palladium.

"Palladium is preferably annealed in nitrogen or carbon monoxide as it oxidizes in air if the temperature is below about 800 °C . . ."

The following annealing procedures, adopted at the National Bureau of Standards, are those suggested by Mr. L. J. Stiles of the General Electric Company. The elements were separated, and the platinum-iridium wire was heated electrically to 1,300 °C (2,372 °F) in air for one minute. Appropriate corrections to observations, made with an optical pyrometer, took account of the emissivity, about 30 percent of the wire. The palladium wire was heated electrically at 750 °C (1,382 °F) for 25 min. Emissivity of the palladium was assumed to be about 35 percent.

The ultimate tensile strength of platinum iridium alloys as given by Carter and Stauss in reference [19] is presented in table 30.

Table 30. *Ultimate tensile strength of platinum-iridium alloys, psi*

Percent Ir	Hard	Annealed
5	70,000	40,000
10	90,000	55,000
15	120,000	75,000
20	145,000	100,000
25	170,000	125,000
30	200,000	160,000

The tensile strength at temperatures up to 1,100 °C of commercial palladium annealed at 1,100 °C, according to reference [18], is given in table 31. The tensile strength of pure palladium that had been annealed at 800 or 900 °C for about five min, according to reference [17], increased from 30,000 psi to 47,000 psi when reduced 50 percent in area by cold drawing.

Table 31. *Tensile strength of commercial palladium at temperatures up to 1,100 °C*

Temperature	Tensile strength, commerical palladium
°C	*psi*
Room	28,000
200	24,500
400	18,100
600	12,700
800	8,300
1,000	3,820
1,100	2,920

Wise, Crowell, and Eash [17] found the proportional limit of commercial palladium to be about 5,000 psi after annealing at 800 °C and 30,000 psi after a 50 percent reduction in area by cold drawing.

Values of resistivity at 20 °C of platinum-iridium alloys and the temperature coefficient of resistance from 10 to 160 °C, from Carter and Stauss [19] are given in table 32. The authors regard these data "as giving good average values of the alloys rather than as giving exact physical constants."

TABLE 32. *Electrical resistivity and temperature coefficient of resistance of some platinum-iridium alloys*

Percent Ir	Resistivity, 20 °C	Temperature coefficient of resistance
	ohms/cmf	10°–160 °C
5	115	0.0020
10	150	.0013
15	170	.0010
20	190	.0008

The electrical resistivity of palladium as determined by Grube and Knabe [56] is given in table 33. Along with this is given the relative resistivity at temperatures up to 800 °C as given by Conybeare [57]. The data presented were taken from reference [9].

TABLE 33. *Electrical resistivity of palladium at temperatures up to 1,400 °C, and relative resistivity up to 800 °C*

Temperature	Resistivity	R_t/R_0	Temperature	Resistivity	R_t/R_0
°C	*ohms/cmf*		°C	*ohms/cmf*	
0	----------	1.000	700	199.7	3.220
100	84.2	1.372	800	214.2	3.449
200	104.7	1.730	900	228.0	----------
300	126.3	2.078	1,000	240.6	----------
400	146.2	2.395	1,200	269.5	----------
500	164.8	2.704	1,400	297.8	----------
600	182.9	2.972			

Resistivity at 0 °C is given by Conybeare as 63.95 ohms/cmf (10.63 microhm-cm), and his value for the α is 0.00372. Vines [9] gives the best value as being about 0.00377 per °C, but does point out that it is dependent upon the temperature used to anneal the palladium.

No direct data have been found on the density of the platinum-iridium alloy, but approximate values may be calculated from the information for platinum and iridium. Vines [9] gives the density of palladium as 11.96 g/cm³ at 18 °C.

No information has been found on the linear coefficient of thermal expansion of the platinum-iridium 15 percent alloy, but a comparison of data in table 34 for the 20 percent iridium alloy with that for platinum in table 12 may be informative. These data are from reference [3], page 151.

TABLE 34. *Coefficient of thermal expansion of the platinum-iridium 20 percent alloy*

Temperature range	Coefficient of expansion $\times 10^6$
°C	*per °C*
0–100	8.3
0–1,000	9.6
0–1,600	10.5

Vines [9] has computed a table of values of the relative length of palladium assuming unit length at 0 °C from the equation of Holborn and Day [58]:

$$l_t = l_0(1 + 1.167 \times 10^{-5}\ t + 2.187 \times 10^{-9}\ t^2)$$

Their value of the linear coefficient of expansion at 0 °C is given as 11.67×10^{-6} per °C. Values of l_t/l_0 are presented in table 35.

TABLE 35. *Thermal expansion of palladium*

Temperature	l_t/l_0	Temperature	l_t/l_0
°C		°C	
0	1.000000	500	1.0064
20	1.000234	600	1.0078
100	1.00119	700	1.0092
200	1.00242	800	1.0107
300	1.0037	900	1.0123
400	1.0050	1,000	1.0139

No data are available on the specific heat of the platinum-iridium 15% alloy. The true (c_p) and mean ($\bar{c}_p$) specific heats of palladium as determined by Jaeger and Veenstra [59] are given in table 36. The mean specific heat is over the range from 0 °C to the upper temperature.

TABLE 36. *True and mean specific heats of palladium*

Temperature	Specific heat cal/g °C		Temperature	Specific heat cal/g °C	
	True	Mean		True	Mean
°C			°C		
0	0.05838	0.05838	700	0.06694	0.06264
25	.05868	.05853	800	.06819	.06326
50	.05898	.05868	900	.06944	.06387
100	.05959	.05898	1,000	.07069	.06449
200	.06080	.05959	1,100	.07195	.06511
300	.06202	.06019	1,200	.07321	.06574
400	.06324	.06080	1,300	.07448	.06636
500	.06447	.06141	1,400	.07576	.06698
600	.06570	.06202	1,500	.07704	.06761

The only information found on the thermal conductivity of a platinum-iridium alloy is from reference [3]; this gives a value for platinum-iridium 10 percent of 0.074 cal/sec/cm²/cm/°C at 17 °C.

Very little is available on the thermal conductivity of palladium. The experimental values given by Hall [60] at 0° and 100 °C are 0.165 and 0.182 cal/sec/cm²/cm/°C respectively.

Information on emissivity of the alloy leg is not available, but indications from the spectral emissivities of platinum and iridium at 0.65 μ are that the emissivity of platinum-iridium should be about 30 percent at this wavelength.

The spectral emissivities of solid palladium at its melting point are, according to reference [3], 38 percent at 0.55 μ and 33 percent at 0.65 μ. Forsythe [61] gives the values of table 37, attributed to Burgess and Waltenburg (1915), of the total emissivity of palladium. These values presumably are for polished, unoxidized palladium.

Neither element of the platinum-iridium 15 percent versus palladium thermocouple is known to be magnetic at room temperature.

TABLE 37. *Total emissivity of palladium*

Temperature	Emissivity
°K	
1,000	0.36
1,400	.33
1,500	.31

d. Platinel Thermocouples

Two types of Platinel [3] thermocouples have been developed by Engelhard Industries, Inc. for use up to 1,300 °C (2,372 °F), about the same range as that for which the platinum-iridium 15 percent versus palladium was designed. These thermocouples are new, and so have not yet been in wide use. A considerable interest has been generated in them, however, to the extent that it seems desirable to include them here.

The negative wire for both thermocouples Platinel No. 1 and No. 2 is a gold-palladium alloy designated by Engelhard as Platinel No. 1503. The positive wires are gold-palladium-platinum alloys designated as Platinel No. 1786 for thermocouple No. 1 and as Platinel No. 1813 for thermocouple No. 2. The exact compositions are proprietary and are not available for publication.

Because little information is available on the properties of these thermocouples, none at all except a provisional reference table being found for Platinel No. 2, the properties at hand are summarized in table 38. These are as supplied by Wilcox and Doring in reference [43]. Temperatures for which these values apply are not given, but presumably determinations for which temperatures are not given are for 0 °C or room temperature. These wires are said to be obtainable in diameters from 0.001-in. up.

TABLE 38. *Properties of Platinel*

Property	Platinel No.		
	1503	1786	1813
Density (calculated)----(g/cm ^{3})--	15.87	13.05	14.91
Resistivity (Hard) ohms/cmf (20 °C)----------	141.0	115	188
Resistivity (annealed) ohms/cmf (20 °C)----------	146.0	117	188
Temperature coefficient of resistance (Hard)------(0–100 °C) (per °C)--	0.0036	0.00183	0.000865
Hardness (BHN, 60 percent reduction)----------	149	----------	----------
Tensile strength (Hard)-----(psi)--	88,360	47,000	98,000
Tensile strength (annealed at 1200 °C)----------	33,000	30,500	47,000
Composition----------	Au, Pd	Au, Pd, Pt	Au, Pd. Pt

The thermal emf of the Platinel No. 1 thermocouple approximates that given in NBS Circular 561 for Chromel-Alumel [4] thermocouples. From work done at the National Bureau of Standards [62] the two temperature-emf relationships cross, the emf of the Platinel becoming the greater at about 850 °F; they cross again at about 1,800 °F. The maximum divergences measured between the Platinel and the NBS table were about 400 μV at 1,400 °F and about 1,050 μV at 2,200 °F. Obviously corrections should be applied for maximum accuracy if values from NBS Circular 561 are used as a reference. A calibration of Platinel No. 1 from reference [43] and one made at the National Bureau of Standards are given in table 39. Provisional data on Platinel No. 2 from reference [43] are included.

TABLE 39. *Calibration of Platinel thermocouples*

Temperature	No. 1		No. 2
	Engelhard	NBS	Engelhard
°C	*Emf mv*	*Emf mv*	*Emf mv*
0	0	0	0
100	3.6	3.55	----------
200	7.6	7.57	----------
300	12.1	11.81	----------
400	16.3	16.25	15.7
500	20.8	20.75	----------
600	25.2	25.20	24.7
700	29.4	29.54	----------
800	33.6	33.68	33.5
900	37.5	37.61	----------
1,000	41.2	41.26	41.7
1,100	44.6	44.70	----------
1,200	48.0	47.86	49.0
1,300	51.1	----------	52.6

The values for No. 1 from Engelhard are given as good to ± 0.1 millivolt (mv) up to 600 °C and to ± 0.2 mv above. No estimate is made as to the accuracy of the NBS results.

Some of the differences between the two calibrations of Platinel No. 1 may have been caused by different annealing treatments before calibration. At the National Bureau of Standards the negative gold-palladium wire was heated electrically at about 2,000 °F (1,093 °C) for 15 min. The positive wire was held at 2,200 °F (1,204 °C) for 15 min. No record is available of the treatment of the thermocouples from which the Engelhard table was devised.

The provisional calibration table over the range 400 to 1,300 °C in reference [43] for Platinel No. 2 differs somewhat from that for Platinel No. 1. Some advantages are claimed for No. 2 over No. 1, but they are not clearly enough defined at this time to give a complete discussion of them.

2.2. Base Metals

Thermocouples discussed in this section are limited to those made of metals and alloys whose usual usable temperature range is considered to be 2,300 °F (1,260 °C) and below. Four ISA types [1] are given in table 40.

Some liberty has been taken in indicating that the second and third thermocouple combinations of table 40 are type K. This designation in reference [1] refers to Chromel-Alumel only;

[3] According to information from Engelhard Industries [43] Platinel is their registered trade mark, and patents on the thermocouples are pending.

[4] Chromel and Alumel are registered trade marks of The Hoskins Manufacturing Co.

TABLE 40. *ISA types of base-metal thermocouples*

ISA type	Trade name or elements	Trade mark of
K	Chromel-Alumel [a]	Hoskins Mfg. Company
K	Kanthal P-N [a]	The Kanthal Corporation
K	Tophel-Nial [a]	Wilbur B. Driver Company
Y [b] and J [c]	Iron-constantan	
Y and J	Iron-Advance [a]	Driver-Harris Company
Y	Iron-Copnic [d]	General Electric Company
J	Iron-Cupron [d]	Wilbur B. Driver Company
T	Copper-constantan [e]	

[a] When so marked in the table this indicates that the names of the alloys are registered trade marks of the companies of the third column.
[b] ISA type Y refers to the tables of NBS Research Paper 1080 [63].
[c] ISA type J refers to the tables of NBS Circular 561 [7]. This is said in reference [1] to be the calibration most widely used today.
[d] Owners of the rights to these names are not known, but these designations are used by the companies listed.
[e] Copper is used in conjunction with Advance, Copnic, Cupron, and constantan, all of which are thermoelectrically similar.

but because claims for properties and performance of the three are similar, it seems reasonable to include Kanthal P–N and Tophel-Nial thermocouples under this type.

The Geminol [5] P–N thermocouple and thermocouples composed of the positive element of the type K and constantan have no ISA designations.

Because some of the elements of this section are paired with more than one other in forming thermocouples, presentation of information is in a different order from that of the section on rare metals. So far as it is practical, data on all thermocouple combinations are given, and properties of the separate elements follow. Also, information available from the proprietors of the thermocouple combinations, when they are known, are given when differences are found between their data and those of suppliers.

a. ISA Type K Thermocouples

Thermocouples of this type that are discussed are those listed in table 40. Among the excellent works on these thermocouples are those of Roeser, Dahl, and Gowens [64]; Dahl [65]; McElroy [11]; Potts and McElroy [66], and Potts and McElroy [77]. Catalog literature is, of course, another source of information, and other references are cited as the need arises.

The usual range of these thermocouples is given by Roeser and Lonberger [6] to be up to 1,100 °C (2,000 °F), and the maximum temperature for them is said to be 1,350 °C (2,450 °F). The makers claim [67, 68, 69] the standard tolerances [1] of ±4 °F (2.2 °C) up to 530 °F (277 °C), and ±¾ percent from 531 °F to 2,300 °F (1,260 °C) are applicable. In addition, thermocouples are offered to meet closer tolerances when needed for precision work. One statement of these tolerances that is available follows in table 41 from reference [67]. In other cases the maximum deviation from the NBS tables is given as one half the standard tolerance of reference [1]. The certified accuracy of calibration at the National Bureau of Standards of base-metal thermocouples (type K in this case)

[5] Geminol is a registered trade mark of the Driver-Harris Company.

TABLE 41. *Special tolerances for different sizes of Chromel-Alumel thermocouple wire*

Wire size	Temperature range	Tolerance
24 to 40 gage	1,000–1,600 °F	±5 °F
18, 20, 22 gage	1,000–2,000 °F	±5 °F

[8] is 1 degree in the range from 0 to 1,100 °C (32 to 2,000 °F). Base-metal thermocouples are not calibrated above 1,100 °C (2,000 °F). The tables for Chromel-Alumel thermocouples in NBS Circular 561 [7] serve as reference tables for all of the type K thermocouples, and the tolerances are in terms of the maximum disagreement with these tables.

The thermoelectric power of the type K thermocouples is about 40 μv per degree C at 0 °C (22 μv/°F at 32 °F) and 36 μv per degree C at 1,260 °C (20 μv/°F at 2,300 °F). Thus the necessity of correcting or compensating for the temperature of the reference junction is obvious in cases where a properly maintained ice bath is not used. Extension wires are furnished for these thermocouples that may be used effectively to extend the thermocouple to the measuring instrument. In the vast majority of industrial installations the measuring instrument is equipped with reference junction compensation so that the only added error from the use of the extension wires is that resulting from the deviation of the calibration of the extension wires from that of the measuring thermocouple. The standard tolerance (limit of error) of the extension leads is given in reference [1] as ±4 °F (2 °C) over the range 0 to 400 °F (−18 to 204 °C). The limits of error of alternate extension wires, of copper-constantan and of iron-alloy, are listed as ±6 °F (3 °C) over the ranges of 75 to 200 °F and 75 to 400 °F, respectively. These limits are said to be for a reference junction temperature of 75 °F only.

Type K thermocouples are available in sizes ranging from No. 2 B&S gage down to No. 40. Maximum recommended operating temperatures from references [67], [68] are given in table 42.

TABLE 42. *Maximum recommended operating temperatures for type K thermocouples*

a. From reference [67]		b. From reference [68]		
B&S gage	Maximum temperature	B&S gage		Maximum temperature
		Minimum	Usual	
	°F			°F
2, 6, 8, and 11	2,300	11	6– 8	2,300
14, 16, and 18	2,000	18	8–11	2,010
20 and 22	1,800	22	11–16	1,830
24 through 40	1,600	38	16–24	1,650

Some suppliers recommend still narrower limits. In one case [70] the range for bare thermocouples is to 2,000 °F for 8-gage and to 1,300 °F for 30-gage wires, and to 2,300 °F and 1,500 °F for the same sizes when protected.

McElroy [11] points out that appreciable inhomogeneities have been found in thermocouples of this type, and that they vary from wire to wire and between producers. The as-received alloys are said to contain mechanical inhomogeneities which are removed to a certain extent by short-time heatings. Much information on this and other phases of use and treatment of, and results to be expected from, the type K thermocouples is found in the comprehensive reports of references [11] and [77].

Dahl [65] conducted stability tests in air on thermocouples among which were the type K. Because of the nature and number of the tests reported in this paper, it is not possible to give detailed results here. The general summarization by Dahl is "From the observations reported it is seen that long-time exposure . . . to high temperatures causes the emf corresponding to a given temperature to increase, or the temperature corresponding to a given emf to decrease." Oxidation of the wires when exposed in 1,000-hr tests to temperatures of 1,800 °F (982 °C) and above was appreciable, to the point that one 8-gage thermocouple oxidized nearly through after 300 hrs exposure to 2,200 °F (1,204 °C). In tests at 1,600 °F (871 °C) and below, oxidation was not enough to materially decrease the diameter of the wires. Potts and McElroy [77] give more recently obtained information on this subject.

Changes in calibrations of 8-gage thermocouples given by Dahl are listed in table 43.

TABLE 43. *Changes in the calibration of Chromel-Alumel (type K) thermocouples heated in air (electric furnace)*

Exposure temperature	Exposure	Maximum change	Exposure temperature	Exposure	Maximum change
°F	hours	°F	°F	hours	°F
800	1,000	<1	1,600	1,000	5
1,000	1,000	<1	1,800	1,000	8
1,200	1,000	+2	2,000	1,000	19
1,400	1,000	3	2,200	200	21

In spite of these apparently adverse findings, type K thermocouples are used successfully in practically all types of industrial operations and control systems suitable to their temperature range. With this, as with any other measurement system, the components must be used intelligently in order to achieve the best performance.

b Geminol Thermocouples

The thermocouple Geminol-P versus Geminol-N was developed, according to the maker [72], to meet the need of the pyrometer industry for a thermocouple to withstand reducing atmospheres. The information presented herein is taken largely from reference [72], because very little information on Geminol is available in the general literature.

The range of Geminol, from the temperature-emf relationship given in [72], is from 0 to 2,300 °F (−18 to 1,260 °C). No NBS reference table has been determined for this thermocouple, but a condensed calibration is given from reference [72] in table 6 of the appendix. The maker claims that the elements are manufactured so that any positive and any negative leg can be combined to be within tolerances of ±4 °F (2 °C) in the range up to 500 °F (260 °C) and ±¾ percent above 500 °F. Geminol extension lead wires with the standard tolerance of ±4 °F (2 °C) in the range 32 to 400 °F are furnished. Geminol was included in the work of Potts and McElroy [77], and a calibration is given by them.

The approximate thermoelectric power of Geminol at several temperatures is given in table 44.

The smallest size wire listed in reference [72] is B & S gage No. 30, and the largest is No. 6.

TABLE 44. *Thermoelectric power of Geminol*

Temperature		Thermoelectric power		Temperature		Thermoelectric power	
°F	°C	μv/°F	μv/°C	°F	°C	μv/°F	μv/°C
20	−7	13.3	23.9	1,000	538	19.1	34.4
100	38	13.6	24.5	1,200	649	20.1	36.2
200	93	14.0	25.2	1,600	871	21.6	38.9
400	204	15.0	27.0	1,800	982	22.1	39.8
600	316	16.6	29.9	2,000	1,093	22.4	40.3
800	427	17.9	32.2	2,200	1,204	22.2	40.0

The thermoelectric power in the table, an average over the 100 °F interval above the listed temperature, increases from 13.3 μv per °F to a constant value of 22.2 at 2,000 °F or a little below From 600 or 800 °F up, however, the change of thermal emf with temperature is comparable to that of type K. Above 1,200 °F the slope of the calibration curve is very close to that of the type K, and the thermoelectric power of Geminol is even a little greater at the top of its usable range.

The low change with temperature of thermal emf in the range near 32 °F is not a disadvantage, because this thermocouple apparently is not designed for use in the low range. It might even be said to provide a small advantage, since the temperature of the reference junction is a little less critical than for the case when the thermoelectric power is constant over the entire range. This advantage, if any, is slight here though, and the usual precautions mentioned earlier about the reference junction should be observed. Extension wires, with the stated limits of error of ±4° up to 400 °F, are available.

Data are presented in reference [72] on the reproducibility of Geminol thermocouples under oxidizing and reducing conditions. The resistance to oxidizing atmospheres from the standpoint of change of thermal emf was examined by cycling the thermocouple to 2,200 °F (1,204 °C) and measuring the resulting changes. No mention of the time of exposure is given. The change at 2,200 °F was comparable with that found for the type K thermocouple by Dahl [65] after exposure to 2,200 °F in air for about 50 hr.

Potts and McElroy [77] concluded that Geminol has superior qualities with respect to drift after

long service at elevated temperatures, and to mechanical strength, or resistance to oxidation.

The thermocouple was subjected to an atmosphere containing 10 percent CO, 5 percent CO_2, 1 percent CH_4, 16 percent H_2, O_2—nil, and the balance N_2, at 1,750 °F (954 °C), conditions chosen to simulate those said to promote "green rot" attack on nickel-chromium alloys in a reducing atmosphere. After 212 hrs the emf at 1,750 °F of two Geminol thermocouples decreased by 0.13 and 0.01 mv, very small changes as compared with those of the "comparison couples" used.

Maximum operating temperatures for the different sizes of Geminol [72] are given in table 45.

TABLE 45. *Maximum recommended temperatures for Geminol thermocouples*

B & S gage	Maximum temperature	B & S gage	Maximum temperature
	°F		°F
30	1,300	18	1,900
28	1,500	14	2,100
24	1,700	8	2,300

c. Iron-Constantan Thermocouples (ISA Types Y and J)

The iron-constantan thermocouple appears to have been the first of the base-metal thermocouples to be accepted on a large scale, and it continues to enjoy wide popularity. Information on this type of sensor is found in references [63, 65, 72], and in catalog literature. In addition, the work of Corruccini and Shenker [73] presents the reference table for iron-constantan that is included in NBS Circular 561 [7], and helps eliminate some of the confusion that had existed regarding the two existing calibrations (ISA types Y and J [1]) for this thermocouple. As mentioned in the footnote to table 40, the type Y thermocouple is that to which the calibration of RP 1080 [63] applies, and the tables of NBS Circular 561 apply to type J. According to Corruccini and Shenker, the type J is the most widely used, but type Y is used exclusively, of the iron-constantan thermocouples, in the field of military aircraft.

The usual range of the iron-constantan thermocouples is given in reference [6] to be −310 °F (−190 °C) to 1,400 °F (760 °C) and the maximum temperature is given as 1,800 °F (982 °C). Suppliers' estimates of the usual range are not consistent, and vary from 1,200 °F (649 °C) for bare B & S 8-gage and 1,400 °F (760 °C) for protected 8-gage wires, to 1,600 °F (871 °C) with no specifications as to size or protection. The maximum service temperature is said in reference [72] to be 1,500 °F in air and 1,750 °F in a reducing atmosphere.

Suppliers generally claim the standard tolerances, or limits of error (deviation from tables of reference [7]), of reference [1], and in this case limits of error for special wires are given in reference [1] as one half the standard. This is so for both thermocouple and extension lead wires. The certified accuracy of calibrations of iron-constantan thermocouples at the National Bureau of Standards [8] is 1 °C.

The thermoelectric power of the iron-constantan thermocouple is about 50 μv per degree C at 0 °C (27 μv/°F at 32 °F), increases to about 54 μv per degree C at 100 °C (30 μv/°F at 212 °F), and 64 μv per degree C at 760 °C (36 μv/°F at 1,400 °F). It is always greater than that of the type K thermocouple, and the type J or Y sometimes is selected because of the supposed increase of accuracy resulting from the greater thermoelectric power. This increase of accuracy is not, however, great enough to be a deciding factor in most cases, and one of the most potent factors in selecting iron-constantan is said to be its lower cost.

Because of the high thermal emf in the normal range of temperature of reference junctions, proper precautions should be taken if extension leads to a compensated measuring instrument are not used.

The iron-constantan thermocouples are available in wire diameters from 0.001 in. up. The maximum size mentioned generally is B & S 8-gage, but apparently larger sizes may be had. Pipe thermocouples also are made of this combination. The outer sleeve, of iron, may be as large as ⅜-in. pipe (about $1\frac{1}{16}$-in. diameter), with the constantan inside in the form of a wire insulated from the pipe and welded to the closed end to form the measuring juntion. This type of thermocouple is described in reference [74].

Recommended upper temperature limits for several wire sizes are given, from three sources, in table 46.

TABLE 46. *Recommended upper temperatures for different wire sizes, iron-contantan*

B & S gage	Upper temperature limits			
	Reference [1]	Reference [70]		Reference [72]
	°F	°F	°F	°F
8	[a]1,400	1,200	[a]1,400	1,500
12	----------	----------	----------	1,300
14	1,100	900	1,100	1,100
16	----------	900	1,100	900
20	900	800	900	700
24	700	650	700	----------
30	700	600	700	500

[a] These columns are given for conditions under which the thermocouples are protected.

Dahl [65] commented:

"The exposure tests on 8-gage iron-constantan thermocouples showed failure of the materials within the 1000-hour heating time for the tests at 1600 °F and above. Failure occurred after 12 hours at 2000 °F, after 28 hours at 1800 °F, and after 300 hours at 1600 °F. The 18-gage iron-constantan thermocouple failed after 500 hours at 1400° F, whereas the 8-gage thermocouple remained serviceable throughout the 1000-hour test at 1400 °F. However, at the conclusion of the test, the diameter of the 8-gage materials had been reduced to about $\frac{1}{10}$ of their original value."

Changes in calibrations of 8-gage thermocouples also given by Dahl are presented in table 47.

TABLE 47. *Changes in the calibration of iron-constantan thermocouples heated in air (electric furnace)*

Exposure temperature	Exposure	Maximum change
°F	hr	°F
800	1,000	<1
1,000	1,000	<1
1,200	1,000	−4
1,400	800	−7
1,600	100	−10
1,800	28	−18
2,000	8	−19

On comparing these changes with the standard tolerances for new wires, they are seen to be well within the standard limits up to 1,600 °F (871 °C), and at 1,200 °F (649 °C) and below, are within even the special limits.

d. Copper-Constantan Thermocouples (ISA Type T)

The copper-constantan thermocouple has been used for a long time, and it still finds favor in the sub-zero and relatively low ranges above 0 °C. Some information on this thermocouple is to be found in references [63, 65, 75, 76] and in the trade literature. The reference tables of NBS Circular 561 [7] are said to be based on the work of Roeser and Dahl [63] which resulted in the so-called 1938 table of Adams.

The usual temperature range, from reference [6], is given as −190 to +300 °C (−310 to +570 °F), and the maximum temperature is cited as 600 °C (1,100 °F). The NBS tables are given up to 400 °C (752 °F) [7]. Generally, 750 °F is the maximum temperature mentioned in catalogs; in some cases this temperature is recommended for intermittent service, and 600 °F (316 °C) is mentioned for continuous use of 20-gage B & S wires. The highest temperature mentioned in connection with copper-constantan thermocouples in reference [1] is 700 °F.

The standard limits of error, from reference [1], are ±1½ °F (0.8 °C) for the range −75 to 200 °F (−59 to 93 °C) and ±¾ percent from 200 to 700 °F (371 °C). Special limits over the same temperature ranges are one half the standard. Extension leads are listed for use over the range −75 to 200 °F, and the limits of error for them are the same as the standard limits for the thermocouple in this range. These same limits of error are given by some suppliers of type T thermocouples.

The thermoelectric power of the copper-constantan thermocouple, from reference [7], is about 21.3 μv per degree F at 32 °F (38.4 μv/°C at 0 °C), 26.0 μv per degree F at 212 °F (46.8 μv/°C at 100 °C), and 33.9 μv per degree F at 700 °F (61.0 μv/°C at 371 °C). This high thermoelectric power is one of the reasons for selection of this thermocouple for accurate work in the lower temperature range above 0 °C, and below 0 down to −200 °C or so. Other reasons will become apparent as properties of the individual elements are given.

These thermocouples are available in diameters from 0.001 in. up. It is probable that, of the base-metal thermocouples, the copper-constantan is used with a reference junction ice bath proportionately more than the others, because it is used in the laboratory and in industrial applications where relatively high accuracies are required.

Recommended upper temperature limits for different wire sizes are given, from two sources, in table 48.

TABLE 48. *Recommended upper temperatures for different wire sizes, copper-constantan*

B & S gage	Upper temperature limits		
	Reference [1]	Reference [70]	
	°F	°F	°F
14	[a] 700	600	[a] 700
16	----------	500	600
20	500	400	500
24	400	400	400
28	400	----------	----------
30	----------	400	400

[a] These columns are given for conditions under which the thermocouples are protected.

No recent detailed information is available on the homogeneity of copper-constantan thermocouples, but from their wide use in the low and sub-zero ranges it seems certain that materials of adequate homogeneity must be available. Dike [76] says that "Copper-constantan thermocouples made of wires taken at random from stock will match the 1938 N.B.S. temperature-emf table for copper against Adams constantan within limits of error of ±0.5 percent or 1.5 deg. F, whichever is larger, between −75 and +200 F. Between 200 and 700 F the limit is ±0.75 percent of the measured temperature. Those limits can be cut in half, or even less, by selecting constantan which matches tabular values more closely."

Because of the high degree of reproducibility of the thermal emf of good copper, the thermal emf of costantan versus platinum is a good indication of the homogeneity of the copper-constantan thermocouple. Roeser and Dahl [63] gave the outputs of thermocouples of three sizes of constantan from the same coil versus Pt 27. Table 49 is the lower half of their table 2 in which this information is presented.

TABLE 49. *Thermal electromotive force of different sizes of constantan wire drawn from the same coil (reference material NBS Pt 27)*

Temperature	Electromotive force (reference junctions at 0 °C)		
	No. 8	No. 14	No. 20
°C	mv	mv	mv
0	0	0	0
100	3.51	3.51	3.50
200	7.43	7.44	7.43
300	11.69	11.70	11.68
400	16.17	16.19	16.16

This table does not necessarily, of course, show the homogeneity of the wire because of the possibility of effects of the rather drastic reductions by drawing of 75 and 96 percent. It does, though, show a maximum difference due to combined causes of 0.03 mv at 400 °C (752 °F). 0.02 mv at 300 °C (572 °F) and only 0.01 mv at 200 °C (392 °F) and below. In each case the difference is, in terms of temperature, well within the prescribed limit of error.

On the assumption that the greater part of the change in service of a copper-constantan thermocouple is due to changes in the constantan wire, Dahl's results [65] on the stability of constantan after periods of heating at 800 °F (427 °C) up to 1,000 hr are of interest. The thermal emf increased 10 μv on exposure for 1,000 hr and 6 μv after 100 hr. These changes, resulting from rather drastic treatment of constantan wires to be used with copper, are not great, and surely should not be so great in normal use for this type of thermocouple.

e. Chromel-Constantan Thermocouples

According to Dike [76] the Chromel-constantan thermocouple is an excellent thermocouple "with excellent properties, both elements being resistant to corrosion and capable of operating at temperatures up to 2,000 °F. It has been used in thermopiles for radiation pyrometers where its high thermoelectric power is of advantage. It is sometimes used in place of Chromel-Alumel in industrial thermocouples."

The tables of NBS Circular 561 [7] for this combination were based on tables for Chromel-platinum in NBS RP 767 [64] and tables for constantan-platinum given in NBS RP 1080 [63]. The thermal emf at 750 °C(1, 382 °F) is given as 57.12 mv as compared with 42.32 and 31.23 mv for iron-constantan and Chromel-Alumel. The approximate thermoelectric power of this thermocouple is given in table 50.

TABLE 50. *Thermoelectric power of the Chromel-constantan thermocouple*

Temperature	Thermoelectric power
°C	μv/°C
0	58.5
200	74.5
400	81.0
600	81.0
800	78.5
1,000	75.0

No limits of error for this thermocouple are given in reference [1].

f. Properties of Base-Metal Thermocouple Materials

The type K wires considered here are the positive Chromel, Kanthal P, and Tophel; the negative wires are Alumel, Kanthal, and Nial. McElroy and Potts, and McElroy [11,77], as mentioned earlier, carried out a very comprehensive investigation of properties including inhomogeneity and drift of Chromel-Alumel and Kanthal P-Kanthal N thermocouples, and included, in addition, "A. C. Scott Chromal and Alumel." Potts and McElroy [66] carried this work further, and described their so-called unilateral temperature gradient furnace and its use in determinations of homogeneity. Dahl's work [65] included determinations of drifts of Chromel and Alumel on exposure to temperatures up to 2,200 °F. The findings are too numerous to give here, and reference to the original papers is suggested. Some inhomogeneities are found in the individual wires and, as may be expected, their outputs drift, depending upon the time and temperature of exposure. The prospective user must therefore decide from the literature the importance in his work of the inhomogeneities and drifts which generally are of such magnitudes as to be relatively unimportant for normal applications.

Compositions of the type K wires, as given by the makers of the first three thermocouples of table 40 are presented in table 51.

TABLE 51. *Compositions of type K thermocouples*

Alloy	Percent of constituents							
	Ni	Cr	Mn	Si	Al	Fe	Co	C
Chromel P[a] [67]								
Kanthal P [68]	90	10						
Tophel [69]	90	9.3		0.4		0.55	0.05	0.03
Alumel [b] [67]								
Kanthal N [68]	98–97			2–3				
Nial [69]	93		2.5	1.05	2.0	0.25	0.50	0.02

[a] "A . . . nickel-chromium alloy containing nearly ten times as much nickel as chromium, but also incorporating nine additional minor constituents . . ."

[b] "It contains nickel, manganese, aluminum and silicon with appreciable percentages of the last three elements . . . plus eight other minor constituents . . . ." Hoskins alloy No. 196 is said by Potts and McElroy [66] to be a nickel-silicon alloy containing between 2 and 3 percent silicon. This, termed Special Alumel, is stated in reference [66] to have given "superior performance." This alloy appears to be similar to the Kanthal N.

Analyses, from several sources, of the type K wires are given in references [11] and [77]. Here the positive elements are seen to contain from about 89 to 90 percent nickel, 9 to nearly 9.5 percent chromium, silicon in amounts up to nearly 0.5 percent and iron from 0.02 to 0.65 percent. Manganese, found in most of the analyses, was present in amounts ranging from 0.01 to 0.8 percent.

Analyses showed the negative elements to be composed of from somewhat less than 94 percent to 96 percent nickel, 1 to 1.5 percent silicon except for Kanthal N which has 2.40 percent, aluminum 1.3 to 2.5 percent, manganese 1.8 to 3.25 percent, and iron and other constituents in smaller quantities. Materials other than nickel and silicon are present in Kanthal in only small amounts. According to Sibley [71], the Special Alumel "meets the guaranteed emf curve for regular Alumel at all temperatures except those within the range from about 100 to 300 °F." On the assumption

that this is alloy No. 196 (table 51, footnote b) or one whose composition is close to it, the negative element of Kanthal is similar, and might be expected to exhibit the same departure from the reference tables. The standard tolerances are as mentioned earlier, listed for Kanthal, and also for Tophel-Nial.

Type K thermocouples find their applications in oxidizing or neutral atmospheres over the higher temperature range up to 2,300 °F (1,260 °C). Even though both elements are subject to oxidation in air above about 1,600 °F (871 °C), they are the most oxidation-resistant of the commonly used conventional base-metal thermocouples. Reducing conditions have adverse effects, and the "green rot," which is associated more with the positive leg of the type K thermocouple than with the negative, is said to be a result of a marginally reducing or oxidizing atmosphere. Chromium is oxidized preferentially and the emf of the wire and consequently of the thermocouple in which it is used is lowered. Environments containing hydrogen, carbon monoxide, and other strongly reducing gases should be avoided.

The negative legs of the type K thermocouples are, as indicated in table 51, of substantially different compositions. None of these alloys seems to be affected by the "green rot" as are the positive legs, but the wires of low silicon content are less resistant to oxidation than are those with more. The increase of silicon seems to increase resistance to oxidation to about the level of that of the positive wire. The low-silicon negative wires are subject to embrittlement by sulfur to the point of breakage; and Sibley [71] said that, from a limited amount of data, the modified (Special) Alumel has provided no improvement in resistance to sulfur.

Potts and McElroy [77] exerted a considerable effort on determination of the effects of cold-working in these alloys, and quotations from their summary follow:

"Generally, the effects realizable from cold work produce calibration shifts of less than 10 °C in nickel-base thermocouples."

"As-received thermocouple wire is generally cold-worked less than 5%."

"Depending on the composition of the alloy, the percentage of cold-working, and the time at temperature, the recrystallization temperature of the nickel-base thermocouple alloys is between 500 and 750 °C. The recovery temperature range is between 250 and 450 °C."

"Heat treatment designed to produce the recovered state in originally cold-worked material causes a recovery of nearly 90% of the error induced by cold-working in Chromel-P and somewhat less in Alumel, principally because the initial change in Alumel is less."

Some physical properties of the type K wires, as given by the makers [67,68,69] are presented in table 52.

Tables have been given by the makers from which the resistance of the positive and negative wires at elevated temperatures may be obtained. Because they are in different forms, tables 53 a, b, and c are given as presented in references [67], [68], and [69].

TABLE 52. *Some physical properties of type K thermocouple wires*

	Chromel P	Alumel	Kanthal P	Kanthal N	Tophel	Nial
Melting point °C	1430	1400	1430	1410	1425	1400
Melting point °F	2605	2550	2605	2570	2600	2550
Resistivity, 20 °C (68 °F) ohms/cmf	425	177	415	133	410	191
Coefficient of resistance $\times 10^4$ per °C, 20–100 °C	3.2	18.8	4.4	30	3.9	24.0
Coefficient of expansion $\times 10^6$ per °C, 20–100 °C	13.1	12.0	14	13.5	13.37	12.25
Specific heat cal/g °C, 20 °C	0.107	0.125	0.11	0.12	0.11	0.12
Thermal conductivity, 100 °C cal/sec/cm²/cm/°C	0.046	0.071	0.05	0.07	0.042	0.064
Density g/cm³	8.73	8.60	8.68	8.69	8.63	8.47
Density lb/in.³	0.315	0.311	0.313	0.314	0.312	0.306
Tensile strength annealed 1,000 psi	95	85	92	72	88	83
Tensile strength, work hardened 1,000 psi	165	170	------	------	------	------
Yield point annealed 1,000 psi	------	------	40	30	30	28
Elongation annealed percent	------	------	22	35	------	------
Magnetic	No	Strong	No	Yes	No	Yes

TABLE 53. *Resistance of type K thermocouple wires at elevated temperatures*

a. Average increase (percent) in resistance when heated

Degrees F	68	100	200	400	600	800	1,000	1,200	1,400	1,600	1,800	2,000
Degrees C	20	38	93	204	315	427	538	649	760	871	982	1,093
Chromel P	0	.67	2.8	7.1	11	14	19	21	24	28	31	34
Alumel	0	4	17	39	51	60	69	78	87	97	107	116

b. To obtain resistivity at working temperature, multiply by factors below

Degrees C	20	100	200	300	400	500	600	700	800	900	1,000	1,100
Degrees F	68	212	392	572	752	932	1,112	1,292	1,472	1,652	1,832	2,012
Kanthal P	1.000	1.035	1.068	1.103	1.144	1.182	1.202	1.226	1.249	1.268	1.305	1.328
Kanthal N	1.000	1.28	1.50	1.64	1.76	1.87	1.98	2.10	2.22	2.35	2.50	2.64

c. Percent change in resistance

Temperature °F	68	100	300	500	700	900	1,000	1,200	1,400	1,600	1,800	2,000
Tophel	0	1	6.5	11	14	17.5	19	22.5	25.5	28.5	31.6	34.5
Nial	0	5.5	37.5	47	55	62.6	66	73.5	80.6	88	95.7	105

Information on the resistance and feet per pound for several sizes of Chromel-Alumel and Kanthal wires is given from references [67] and [68] in table 54.

TABLE 54. *Resistance and length per pound of several sizes of Chromel-Alumel and Kanthal wires*

B & S gage	Wire diameter	Ohms per ft at 68 °F				Approximate ft/lb
		Chromel P	Alumel	Kanthal P	Kanthal N	
	in.					
8	0.1285	0.0257	0.0107	0.0252	0.00806	21
14	.0641	.104	.0432	.101	.0324	83
16	.0508	.164	.0681	.161	.0516	131
20	.0320	.415	.173	.407	.130	332
24	.0201	1.05	.438	1.03	.329	839
28	.0126	2.68	1.12	2.61	.836	2,130
30	.0101	4.25	1.77	4.07	1.30	3,320
36	.0050	17.1	7.12	16.6	5.32	13,600
40	.0031	45.4	18.5	43.2	13.8	35,300

The thermal coefficients of expansion at various temperatures of Tophel and Nial [69] are given in table 55.

TABLE 55. *Thermal coefficient of expansion of Tophel and Nial*

	Thermal coefficient of expansion, in./in. °C×10⁶, 20 °C to temperature								
Temperature, °C	20	100	200	300	400	500	600	700	750
Tophel	----	13.37	13.94	14.36	14.74	15.15	15.59	16.05	16.26
Nial	----	12.25	13.06	13.79	14.21	14.67	15.05	15.50	15.69

The specific heat at elevated temperatures of the nickel 80 percent-chromium 20 percent alloy, from reference [92] is given in table 56.

TABLE 56. *Specific heat of 80 percent Ni–20 percent Cr*

Temperature	Cal/g °C	Temperature	Cal/g °C
°C		°C	
0	0.1033	400	0.1264
25	.1052	500	.1310
50	.1071	600	.14
100	.1109	700	.1470
200	.1171	800	.1515
300	.1217	900	.1563

Information from reference [69] in table 57 shows the change of thermal conductivity of Tophel and Nial with temperature.

TABLE 57. *Thermal conductivity of Tophel and Nial*

	Thermal conductivity, cal/sec/cm²/cm/°C at temperature								
Temperature °C	20	100	200	300	400	500	600	700	750
Tophel	0.042	0.047	0.052	0.058	0.063	0.068	0.073	0.078	0.080
Nial	0.064	0.063	0.070	0.077	0.084	0.090	0.096	0.102	0.104

The only type K wires for which the thermal emfs against platinum are found are Chromel and Alumel. Tables of thermal emf for these alloys from reference [77] are given in table 58.

TABLE 58. *Calibrations for Chromel-platinum[a] and Alumel-platinum[b] thermocouples*

Temperature	Chromel	Alumel	Temperature	Chromel	Alumel
°C	*emf, mv*	*emf, mv*	°C	*emf, mv*	*emf, mv*
0	0	0	700	22.9610	6.1835
100	2.8110	1.2885	800	26.2240	7.0820
200	5.9695	2.1640	900	29.4115	7.9530
300	9.3260	2.8860	1,000	32.5320	8.7850
400	12.7655	3.6335	1,100	35.5830	9.5785
500	16.2150	4.4310	1,200	38.5475	10.3420
600	19.6245	5.2875	1,300	41.4005	11.0660

[a] Based on Hoskins Mfg. Co. Table E-271-CC.
[b] Based on Hoskins Mfg. Co. Table E-271-AA.

This table is condensed from the original in which the intervals are 10 °C. According to the authors, values of their table for the Chromel-Alumel thermocouple may depart from those of NBS Circular 561 by as much as 10 μv. No statement is found about the identity of the reference platinum used, but presumably the data of table 58 are given against NBS Pt 27 or against a specimen of low thermal emf versus Pt 27.

Little if any definitive information is found on emissivity of the type K wires. Roeser and Wensel give on page 1313 of reference [20] the emissivity of unoxidized Chromel P at a wavelength of 0.65μ to be 0.35, and that for Alumel to be 0.37. The probable value at the same wavelength for oxide formed on smooth Chromel P and Alumel is given as 0.87. Later, on page 1315, the total emissivity of oxidized 80 percent nickel-20 percent chromium is given as 87 percent at 100 and 600 °C and 89 percent at 1,300 °C. The warning is given here that "Most values are uncertain by 10% to 30%. In many cases value depends upon particle size." Emissivity at room temperature (presumably total) is given in reference 70 as 0.64 to 0.76 for Chromel P and 0.60 to 0.75 for Alumel.

The Geminol wires are the positive Geminol P, said in reference [72] to comprise 20 percent chromium, 1 percent columbium (niobium), and the balance nickel, and the negative leg containing 3 percent silicon in nickel. Analyses presented by McElroy [11] show Geminol P, 20-gage and 24-gage wires, to contain nickel 78.67 and 79.03 percent, chromium 17.92 and 18.07 percent, silicon 0.74 and 0.85 percent, iron 0.73 and 0.76 percent, columbium 0.99 and 0.94 percent, and copper 0.02 and 0.03 percent. Geminol N of the same sizes is reported to comprise nickel 96.43 and 96.78 percent, and silicon 2.75 percent, columbium 0.05 percent, carbon 0.01 percent, and chromium 0.005 percent in each.

Reference [77] points out the superiority of both Geminol wires under adverse conditions over the type K. The higher chromium content of the positive leg and the greater percentage of silicon in the negative leg are indicated as the responsible factors. This comparison does not include Chromel-Special Alumel, but it does include Kanthal N with 2.40 percent silicon as opposed to 2.75 percent silicon in Geminol N.

Among features claimed by the makers for Geminol P are its "unexcelled oxidation resistance," and resistance to "green rot." The negative leg has a resistance to oxidation that is comparable with that of the positive wire of the type K thermocouples. According to the makers, the Geminol thermocouple is resistant to change of calibration when used under at least some reducing conditions. The separate wires are said to be made to close enough tolerances that any Geminol P, connected to any Geminol N, will provide a thermocouple having a calibration within the standard limits of error.

Some physical properties of Geminol P and N from reference [72] are given in table 59.

Except for conversion of the value for thermal conductivity from watts to calories per second, the values of the table are as given. No temperatures

Table 59. *Some physical properties of Geminol P and Geminol N*

Property	Geminol P	Geminol N
Melting point, °C	1,400	1,420
Melting point, °F	2,552	2,588
Resistivity, ohms/cmf (20 °C)	655	162
Coefficient of resistance × 10^4, per °C	11	24
Coefficient of expansion × 10^6, per °C	17	14.5
Thermal conductivity, cal/sec/cm²/cm/°C (100 °C)	0.0267	0.0907
Weight, lb/in.³	0.034	0.311
Specific gravity	8.41	8.60
Magnetic strength	None	Strong

are given in the reference, but from another table in the same reference it seems reasonable that the temperatures inserted in the "property" column apply. Other temperatures that seem to apply to the values in the table are the range 20 to 500 °C for the temperature coefficient of resistance of Geminol P, 20 to 100 °C for that of Geminol N, 10 to 1,000 °C for the coefficient of expansion of the P wire, and 20 to 500 °C for the Geminol N. The tensile strength at 20 °C is given as maximum and minimum of 200,000 and 100,000 psi for an alloy close in composition to Geminol P, and 150,000 and 75,000 for an alloy having a composition near that of Geminol N. The specific heat of these same two alloys is given as 0.104 and 0.128 cal/g °C. No temperature for which these values apply is given.

Information on the resistance and feet of wire per pound of Geminol P and N in table 60 is taken from reference [72].

Table 60. *Resistance and length per pound of several sizes of Geminol P and Geminol N wires*

B&S gage	Wire diameter	Ohms per foot		Approximate ft/lb
		Gem. P	Gem. N	
	In.			
8	0.1285	0.0400	0.00989	21
14	.0641	.160	.0395	85
16	.0508	.252	.0623	134
20	.0320	.640	.158	341
24	.0201	1.62	.401	864
28	.0126	4.12	1.02	2,200
30	.0101	6.55	1.62	3,490

The thermal emf of the Geminol wires versus Pt 27 is tabulated in reference [72]. This is reproduced in table 61.

Table 61. *Thermal emf of Geminol P and Geminol N versus* Pt *27*

Temperature	Geminol P versus Pt 27	Geminol N versus Pt 27	Temperature	Geminol P versus Pt 27	Geminol N versus Pt 27
°F	*mv*	*mv*	°F	*mv*	*mv*
32	0.00	0.00	1,200	+12.70	−6.35
200	+1.22	−1.04	1,400	+15.66	−7.44
400	+3.11	−1.96	1,600	+18.74	−8.56
600	+5.24	−2.94	1,800	+22.00	−9.65
800	+7.27	−4.09	2,000	+25.43	−10.65
1,000	+9.96	−5.24	2,200	+28.80	−11.75

No information is available on the emissivity of these wires, but it seems reasonable that the values given for the type K wires should at least approximate those for Geminol.

Thermocouple iron, unlike materials discussed previously, is not normally made expressly for thermocouples, but is obtained by selection from lots of pure iron made for other purposes. Differences between lots of iron appear to have become less since the introduction of the iron-constantan thermocouple, though, and by selection of both the iron and constantan wires it is possible to provide thermocouples to match the ISA type J or type Y tables. This is done to the extent that, accordlng to Dike [76], "Well over two hundred tons of these thermocouples are supplied to industry annually in the U.S."

Originally, according to Dike, the use of iron in thermocouples was opposed strongly by authorities in the field of thermoelectric pyrometry because of the inhomogeneity of the iron wire obtainable. This objection has been overcome, and its popularity has survived because of its large thermoelectric power with constantan, its adaptability to use under both oxidizing and reducing conditions, and its low cost.

Much of the information that follows on properties of iron has been taken from reference [26] and the monograph of Cleaves and Thompson on iron [78]. Although no assurance exists that the iron for which properties are given matches that of thermocouple wire, the information presented here is for commercially pure or electrolytic iron which should be expected to be fairly representative of thermocouple iron.

Analyses of the iron wires used in determination of the modified 1913 reference tables of NBS Circular 561 [7] by Corruccini and Shenker [73] are given in table 62.

Table 62. *Chemical and spectrographic analyses of iron samples*

Values are given in percent.

Sample	C	Mn	P	S	Cu	Si [a]	Ni [a]	Cr [a]	Sn [a]
A-1	0.07	0.25	0.015	0.031	0.12	<0.01	0.044	0.015	<0.01
C-1	.11	.38	.005	.031	.054	<.01	.030	.016	<.01
D-1	.04	.29	.009	.024	.14	<.01	.042	.016	<.01
F-1	.02	.03	.004	.029	.15	<.01	.039	.025	<.01
F-3	.08	.43	.080	.028	.018	.02	.011	<.01	.01
F-4	.02	.23	.011	.016	.023	<.01	.014	<.01	<.01
F-5	.06	.21	.006	.020	.022	.01	.013	<.01	<.01
F-6	.05	.22	.006	.018	.022	<.01	.012	<.01	.01

[a] Spectrographic determination.

From reference [78], exposure of a fresh surface of iron to air, in the absence of moisture, causes a rapid development of a superficial coating of iron ioxide. At temperatures below 150 °C (302 °F), the coating is said to be so thin as to be invisible, but suffices to prevent further oxidation. At temperatures above 200 °C (392 °F) the rate and extent of reaction between iron and air increase with temperature. Liquid water, even though only an adsorbed film, is said to be neces-

sary for corrosion in the atmosphere, and rusting is speeded up by temperature fluctuations causing condensation from the surroundings. Rusting may result from wet steam, and according to Cleaves and Thompson, iron may be attacked appreciably by atmospheres of hydrogen, nitrogen, or ammonia.

A statement from reference [78] summarizing the information on corrosion of iron in aqueous solutions follows:

"Even the purest iron dissolves to a slight extent in pure water in the absence of oxygen and rusts in pure water in the presence of oxygen. In general iron is subject to corrosion in aqueous solutions of acids, alkalies, and salts. The rate and extent of corrosion vary with a number of factors including hydrogen-ion concentration, presence of oxygen, agitation, temperature, and nature and concentration of the solution. Some degree of protection may result from passivity or from the formation of protective films but these factors, and the effect of purity and homogeneity in the metal, are usually of slight importance in submerged corrosion."

In connection with the popularly held conception that pure iron is markedly corrosion resistant, Cleaves and Thompson say that.

"The effect of purity, in comparison of very pure irons with commercial products or in comparison of different grades of commercial products one with another, usually is less important than the effect of external conditions. Real resistance to corrosion is obtained only by the incorporation of considerable amounts of added elements, such as silicon in cast irons or chromium and nickel in stainless steels, but even these products are not universally resistant to corrosion. The corrosion resistance of iron may be summarized in two words—iron rusts."

The melting point of iron is, from reference [3], 1,533 °C (2,791 °F).

Information on the tensile properties of iron, even in its purer states, is widely divergent. Much information is avilable, but selection of data that apply strictly to thermocouple iron is practically impossible. The summary of data on tensile properties from reference [78] follows:

"Available information indicates that electrolytic iron in the as-deposited condition may have tensile strengths and yield strengths of more than 100,000 lb. per sq. in. with elongations as small as 3 per cent. However, the properties of the same material in the annealed condition are roughly comparable to those of Armco iron. The tensile strength of annealed electrolytic iron is reported to be between 40,000 and 55,000 lb. per sq. in., yield strength between 20,000 and 25,000 lb. per sq. in., with elongations between 25 and 45 per cent. Fusion in vacuum with subsequent annealing treatment further softens electrolytic iron. The reported properties of such material are: tensile strength between 35,000 and 40,000 lb. per sq. in., yield strength between 10,000 and 20,000 lb. per sq. in. elongation between 30 and 60 per cent, and reduction of area between 70 and 90 per cent."

The Armco iron mentioned above is described as one of the commercially pure types. The temperature of annealing that caused the reduction in tensile strength of the electrolytic iron is not specified definitely, but annealing for 1 hr up to 300 °C (572 °F) had no effect. Several annealing temperatures in the range from 900 °C (1,652 °F) to 960 °C (1,760 °F) are listed.

The variations of tensile strength and modulus of elasticity of Armco iron with temperature are given in table 63.

TABLE 63. *Variation of tensile strength and modulus of elasticity of Armco iron with temperature*

Temperature		Tensile strength	Elastic modulus
°C	°F	psi	psi × 10³
0	32	44,400	29,000
100	212	30,300	28,100
200	392	30,700	25,700
300	572	45,700	22,200
400	752	34,300	------
500	932	21,500	------
600	1,112	11,800	------
700	1,292	7,800	------
800	1,472	3,700	------
900	1,652	3,900	------
1,000	1,832	5,700	------

The above values from reference [78] and attributed to Lea [79] are taken from a small-scale curve and so must be considered to be approximations.

Hardness of the specimens used in the work of reference [73] is given in table 64.

TABLE 64. *Results of hardness measurements on samples of iron wire*

Sample	Vickers number [a]	Equivalent Rockwell B number	Sample	Vickers number [a]	Equivalent Rockwell B number
A–1	99.8	55	F–3	210	94
C–1	106	59.5	F–4	83.6	39
D–1	138	76	F–5	138	76
F–1	127	71	F–6	131	73

[a] Determinations were made with a 10-kg load applied through a square-based diamond pyramid-indenter.

The resistivity of iron relative to that at 0 °C (32 °F), from reference [20], is given in table 65. Some values of the table have been adjusted slightly to bring them more nearly into agreement with the International Temperature Scale of 1948. Information on resistivity is presented in some detail in reference [78].

TABLE 65. *Electrical resistivity of iron relative to the resistivity at 0 °C* (R_t/R_0).

[The actual resistivity (ohms/cmf) is given for 0 °C].

Temperature		R_t/R_0	Temperature		R_t/R_0
°C	°F		°F	°F	
0	32	1.000	500	932	6.162
0	32	(51.56)	600	1,112	7.839
100	212	1.650	700	1,292	9.785
200	392	2.454	800	1,472	12.000
300	572	3.485	900	1,652	12.787
400	752	4.716	1,000	1,832	13.069

The suggested value for the density of pure iron at "room temperature" in reference [78] is 7.87 g/cm³ (0.2843 lb/cu in.).

The thermal coefficient of expansion of electrolytic iron is given in reference [80]. Both the relative length at elevated temperatures and the

true thermal coefficient of expansion are given in table 66.

Additional information on different high-purity irons is found in references [26] and [78].

True and mean specific heats of electrolytic iron from reference [80] are given in table 67.

A large quantity of information on thermal conductivity of iron is found in reference [26], and table 68 gives values obtained at Battelle [81] for Armco iron of 99.906 percent purity.

Averages of the values of the thermal emfs for the eight samples of iron versus Pt 27, from reference [73], are given in table 69.

Although a considerable amount of information is found on the emissivity of iron, large differences exist between different observers for conditions that apparently are similar. Wilkes [82] gives the total normal emissivity of iron to be 0.05 and 0.07 at 100 and 500 °F. This is in fair agreement with values from McAdams [83], of 0.052 to 0.064 over the temperature range from 350 to 440 °F. For polished iron the total normal emissivity ranges from 0.144 to 0.377 over the range 800 to 1,800 °F. Wrought iron, highly polished, is reported as having an emissivity of 0.28 over the range from 100 to 480 °F.

Smooth oxidized electrolytic iron, according to McAdams, has a total normal emissivity in the range 260 to 980 °F varying from 0.78 to 0.82. Oxidized iron at 212 °F has an emissivity of 0.736. Emissivities of 0.85 to 0.89 are given for iron oxide over the range 930 to 2,190 °F.

The emissivity of electrolytic iron was determined by Wahlin [84] to be approximately 0.345 from about 1,000 to near 1,178 °K, then decreased to 0.325 at 1,178 °K (A_3 point) with a dip to approximately 0.318 at about 1,360 °K. The emissivity increased to about 0.325 near 1,677 °K and 0.338 at 1,677 °K (A_4 point). This work was done with an optical pyrometer and so the spectral region presumably was near 0.65 or 0.66 μ. The total emissivity of iron (black) at 200 °F is reported by McDermott [85] to be 0.56, and McAdams [83] gives 0.657 for the same temperature. Roeser and Wensel [20] give 0.35 at 0.65 μ for unoxidized iron, and 0.87 for the probable emissivity at 0.65 μ of the oxide formed on smooth cast iron.

Copper, from the standpoint of utility in thermocouples, has some unusually desirable features. Thermoelectric properties of the commercial metal are exceptionally uniform, and mishandling resulting in severe cold working does not produce the large thermoelectric changes that it does in some other materials. Roeser and Dahl [63] found a total spread of 29 μv, with junctions at 0 and 350 °C, in the emf of 31 samples of copper ranging from 8-gage B & S to 40-gage. Differences amounting to only 24 μv between cold-rolled and annealed wires, with junctions at 0 and 300 °C have been encountered by others. Results on copper drawn from a rod of one-half inch diameter to sizes from 8-gage to 22-gage show the maximum difference between the cold-worked and annealed

TABLE 66. *Thermal expansion of electrolytic iron*

t	Coefficient of expansion	l_t/l_0	t	Coefficient of expansion	l_t/l_0	
°C	×10⁶ per°C		°C	×10⁶ per°C		
0	----------	1.000000	325	15.39	1.004341	
100	12.62	1.001158	350	15.54	1.004725	
110	12.67	1.001284	375	15.74	1.005114	
120	12.76	1.001411	400	15.88	1.005507	
130	13.32	1.001539	425	16.01	1.005904	
140	14.25	1.001672	450	16.17	1.006304	
145	13.32	1.001743	500	16.37	1.007115	
150	13.12	1.001810	550	16.47	1.007935	
160	13.56	1.001941	600	16.61	1.008762	
170	13.82	1.002076	650	16.64	1.009592	
180	14.02	1.002146	700	16.68	1.010424	
190	14.14	1.002355	732	----------	1.010884	
200	14.32	1.002496	733	----------	1.010827	Shrinkage
225	14.54	1.002853				
250	14.78	1.003217	736	----------	1.010669	
275	14.97	1.003587	750	20.97	1.010972	
300	15.20	1.003961	770	20.95	1.011390	
			800	20.97	1.012018	

TABLE 67. *True mean specific heats of eletrolytic iron*

a. True specific heat				b. Mean specific heat		
t	Cal/g °C	t	Cal/g °C	t	t'	c_p between t and t'
°C		°C		°C	°C	cal/g °C
105	0.112	850	0.190	100.3	21.267	0.1127
150	0.132	900	0.182	200.2	21.861	0.1161
200	0.123	975	0.142	301.2	22.996	0.1202
250	0.134	1,000	0.144	402.4	22.673	0.1256
300	0.136	1,050	0.148	500.4	23.453	0.1312
350	0.143	1,100	0.151	605.0	23.172	0.1386
400	0.146	1,150	0.156	707.9	24.458	0.1467
450	0.151	1,200	0.162	770.3	25.442	0.1557
500	0.160	1,250	0.169	825.1	24.846	0.1597
555	0.169	1,300	0.176	910.1	25.260	0.1623
600	0.175	1,350	0.178	1,067.5	24.144	0.1644
650	0.186	1,400	0.180	1,197.2	24.212	0.1635
700	0.213	1,450	0.200	1,391.1	25.375	0.1651
750	0.281	1,500	0.200	1,403.9	25.032	0.1662
800	0.213	----------	----------	1,491.1	25.598	0.1686

TABLE 68. *Thermal conductivity of Armco iron*

Temperature	cal/sec/cm²/cm/°C	Temperature	cal/sec/cm²/cm/°C
°C		°C	
0	0.180	600	.095
100	.162	700	.086
200	.146	800	.079
300	.132	900	.083
400	.118	1,000	.086
500	.106		

TABLE 69. *Thermal emf of iron verse Pt 27*

Temp.	Emf	Temp.	Emf
°F	mv	°F	mv
32	0.00	1,000	7.03
100	0.67	1,100	7.63
200	1.64	1,200	8.31
300	2.56	1,300	9.11
400	3.41	1,400	10.04
500	4.16	1,500	11.04
600	4.82	1,600	12.02
700	5.47	1,700	12.86
800	5.96	1,800	13.67
900	6.48		

copper, with the junctions at 0 and 350 °C, to be 9 μv. According to Dike [76], copper need not be specially selected for thermocouple use if it conforms to ASTM Spec. B3–45 for soft or annealed bare copper wire.

A disadvantage which restricts the use of copper in thermocouples generally to temperatures of 400 °C (752 °F) and below is its oxidation at relatively low temperatures. Its high thermal conductivity may be advantageous in some instances, but additional care is required when using copper to insure that both the measuring and reference junctions assume the desired temperatures. Copper wire is available in diameters from 0.001 in. up, and because of its higher thermal conductivity (about 20 times that of Chromel P) and electrical conductivity (about 40 times that of Chromel P) often is used in smaller sizes than are other wires.

Copper is extremely resistant to corrosion under normal atmospheric conditions; and according to Gilbert, page 380 of reference [86], its good behavior depends to a considerable extent on the maintenance of an inhibitive film of oxide or other insoluble corrosion product. Corrosion resistance of copper, unlike that of some other metals, is not influenced by the grade or impurities present. Copper is said to be "usually virtually unattacked in most non-oxidizing solutions", and under fairly mild conditions copper is successfully used for handling solutions of hydrofluoric, hydrochloric, sulfuric, phosphoric, and acetic and other fatty acids. Increased concentration, temperature, and flow rate cause increased corrosion. Copper is said to be attacked to some extent by aerated alkaline solutions, and its use should be avoided where ammonia is present. It is unsuitable for use in hydrogen peroxide and in molten sulfur, and corrosion is accelerated by hydrogen sulfide. Sulfur dioxide is corrosive at high relative humidity (about 65 percent), and becomes more so with an increase of concentration.

The mechanical properties of copper are affected by a wide variety of conditions, and so it is not possible to give a complete picture of them here. Some of these properties presented by Smart in reference [86], page 374, are listed in table 70.

TABLE 70. *Some comparative stress-strain relations of tough-pitch and oxygen-free copper*

Property	Tough-pitch Cu		Oxygen-free Cu	
	Hard	Annealed	Hard	Annealed
Modulus of elasticity——psi×10⁻⁶	16.95	15.82	17.54	16.20
Yield strength (0.5 percent strain) psi	46,000	5,500	47,000	5,000
Tensile strength——psi	46,900	31,500	47,500	30,900
Elongation in 2 in——%	14.8	53.0	20.5	60.0
Reduction of area——%	58.5	71.4	86.4	92.1

According to Smart, "High purity copper is so ductile that it is difficult to determine the existence of a finite limit beyond which it cannot be cold worked. No evidence of such a limit has been observed in wires drawn 99.4 percent . . . ."

According to Jennison and Smith [87], perfectly pure copper, under extended periods of annealing, will recrystallize at about 212 °F. Smart, however, gives on page 413 of reference [86] a table of softening temperatures of pure copper with individual impurity additions. Some of his data are presented in table 71.

TABLE 71. *Softening temperature (degrees C) of pure copper containing individual impurity additions*

Samples annealed ½ hr at 600 °C (1,110 °F) prior to final cold reduction of 75 percent.

Softening temperature of pure copper=140 °C (284 °F).

Quantity / Impurity	0.002 percent		0.005 percent	
	T.P.[c]	O_2-free	T.P.	O_2-free
O_2	140	140	140	140
Fe	140	146	140	153
Sh[a]	180	192	258	282
As	168	168	189	189
Ni	140	140	140	140
Pb[a]	146	250	146	270
Bi[a]	210	260	247	300
Ag	148	148	172	172
Sn	140	198	140	277
S[b]	181	181	183	183
Se[b]	222	222	234	234
Te[b]	212	212	228	228
P	140	258	140	284
Si	----------	161	----------	181
Co	----------	145	----------	152
Cr	----------	152	----------	190
Zn	----------	148	----------	151
Cd[a]	----------	183	----------	248

[a] Copper containing oxygen in the tough-pitch range.
[b] Tough-pitch values reflect partial oxide formation. Values equivalent to those given for oxygen-free copper can be obtained by heat treatment at temperatures in excess of 700 °C (1,290 °F).
[c] Much higher values obtainable by heat treatment to increase solid solubility.

Some physical properties of copper are summarized in table 72, taken from a table by Smart, page 363, reference [86].

TABLE 72. *Some physical properties of copper*

Melting point, 1083° ± 0.1 °C
1981.4° ± 0.2 °F
Coefficient of thermal expansion at 20 °C, 0.0000165 per °C; for 0 to 300°C, $L_t = L_0[1 + (16.23t + 0.00483t^2) \times 10^{-6}]$
Specific heat at 20 °C, 0.092 cal/g °C
Specific heat, solid, 0 to t °C, 0.092 + 0.0000250t cal/g °C
Thermal conductivity at 20 °C, 0.934 cal/sec/cm²/cm/°C (adjusted to electrical conductivity of 101 percent
Resistivity at 20 °C,[a] 1.7241×10^{-6} ohm cm, 10.371 ohms/cmf
Temperature coefficient of electrical resistivity at 20 °C, 0.00394 per °C
Emissivity,

At wave length μ	0.70	0.65	0.60	0.55	0.50
Percent ε at 1,000 °C (1,932 °F)	8.7	11.2	18.5	31.3	40.4
Percent ε at 1,125 °C (2,057 °F)	11.8	14.8	20.5	29.3	38.7

[a] IACS copper, 100 percent, 0.15328 ohm at 20 °C (meter gram).

A table of factors to reduce the resistivity of 96 to 100 percent conductivity and at temperatures from 0 to 75 °C is given on page 407 of reference [3].

TABLE 73. *Electrical resistivity of copper relative to the resistivity at 0 °C (R_t/R_0)*

The actual resistivity (ohms/cmf) is given for 0 °C.

Temperature		R_t/R_0	Temperature		R_t/R_0
°C	°F		°C	°F	
0	32	1.000	500	932	3.210
0	32	(9.38)	600	1,112	3.695
100	212	1.431	700	1,292	4.208
200	392	1.862	800	1,472	4.752
300	572	2.299	900	1,652	5.334
400	752	2.747	1,000	1,832	5.960

TABLE 74. *True and mean thermal coefficients of expansion of copper*

Temperature	Expansion coefficient $\times 10^6$		Temperature	Expansion coefficient $\times 10^6$	
	True at $t°$	Average, 0° to $t°$		True at $t°$	Average, 0° to $t°$
°C			°C		
0	16.73	--------	600	20.63	18.63
100	17.27	17.00	700	21.46	19.01
200	17.83	17.29	800	22.33	19.41
300	18.45	17.60	900	23.25	19.83
400	19.13	17.92	1,000	24.16	20.26
500	19.85	18.27			

The resistivity of copper relative to that at 0 °C (32 °F) from reference [20] is given in table 73.

A standard density at 20 °C of 8.89 g/cm³ (0.321 lb/cu in.) was adopted for copper of 100 percent conductivity. Smith [88], however, accepts 8.94 g/cm³ (0.323 lb/cu in.) as the density of annealed pure copper.

The true and average thermal expansion of copper, from reference 23, follow in table 74. The length of a heated piece of copper, l_t, is given as:

$$l_t = l_0(1 + 16{,}733 \times 10^{-6}t + 0.002626 \times 10^{-6}t^2 + 0.00000091 \times 10^{-6}t^3).$$

True and mean specific heats of electrolytic copper as given by Jaeger, Rosenbohm, and Bottema are presented in table 75. The equation for the total heat content Q_0 at temperature $t°$ C is

TABLE 75. *True and mean specific heats of copper*

Temperature	Specific heat, cal/g °C	
	True, at t°	Mean, 0° to t°
°C		
300	0.0988	0.0957
400	.1009	.0968
500	.1030	.0978
600	.1051	.0988
700	.1072	.0999
800	.1092	.1009
900	.1113	.1020

$$Q_0 = 0.092597t + 0.10416 \times 10^{-4}t^2,$$

for the true specific heat c_p,

$$c_p = 0.092597 + 0.20832 \times 10^{-4}t,$$

and for the mean specific heat above 0 °C, $\bar{c}_p$ is

$$\bar{c}_p = 0.092597 + 0.10416 \times 10^{-4}t.$$

The thermal conductivity of copper, from Smith [88], is given in table 76.

TABLE 76. *Thermal conductivity of copper*

Temperature	Thermal conductivity
°C	cal/sec/cm²/cm/°C
0	0.912
20	.910
100	.901
200	.890
300	.879
400	.867
500	.856
600	.845

The thermal emf of copper relative to platinum, from Roeser and Wensel [20], is given in table 77.

TABLE 77. *Thermal emf of copper relative to platinum*

Temperature		Emf	Temperature		Emf
°C	°F	mv	°C	°F	mv
0	32	0	600	1,112	8.34
100	212	0.76	700	1,292	10.49
200	392	1.83	800	1,472	12.84
300	572	3.15	900	1,652	15.41
400	752	4.68	1,000	1,832	18.20
500	932	6.41			

Constantan is a name applied to a family of copper-nickel alloys most of which were designed originally to provide wires having a low temperature coefficient of resistance. According to Dike [76] the composition ranges from copper 50 percent–nickel 50 percent to copper 65 percent–nickel 35 percent, with small percentages of manganese and iron as well as some trace impurities, such as carbon, magnesium, silicon, cobalt, etc. The precise composition is not specified; but it depends upon the use to which the alloy is to be put, such as to match thermoelectrically a particular iron for an iron-constantan thermocouple, or to be used with copper or a positive type K element to match particular thermocouple tables. According to Roeser and Dahl [63] "Constantan . . . includes the alloys made in this country under such trade names as Advance (Ideal), Copel, Copnic, Cupron, etc., most of which contain approximately 55 percent of copper and 45 percent of nickel."

The approximate melting point of constantan, although not a limiting factor in its use in thermocouples, is given as 1,210 °C for Advance [72], an alloy of copper 57 percent–nickel 43 percent.

The stability of constantan was pointed out by Dahl [65]. After 1000 hrs of heating in air at 800 °F (427 °C), which is above the recommended temperature for the copper-constantan thermocouple, the change in 8-gage constantan at 800 °F corresponded to only about 0.5 °F. This is well within the tolerances for the copper-constantan thermocouple, and since copper is highly reproducible, this is the drift that might be expected from prolonged use of this thermocouple in its extreme range.

On heating 8-gage constantan in air to 1,800 °F, it was found to deteriorate to the point of imminent failure after 28 hrs. The life of the iron wires used was about the same as that of the constantan. The maximum change in the constantan wire corresponded to about an increase of 13° at 1,200 to 1,400 °F and the change decreased to about 8° at 1,800 °F. The maximum change is greater than the allowable limit of error for new thermocouples; and when the constantan was coupled with the iron used, the change in the iron, corresponding to a decrease of about 9° at 1,800 °F, gave a net decrease of emf at 1,800° that corresponded to about 17 °F. After exposure for 200 hrs to 1,600 °F, the increase of the emf of the constantan corresponded to about 10° at 1,600 °F and the decrease of the iron to about 10 °F; the net decrease of emf at 1,600° thus was about 20 °F.

As mentioned above, constantan oxidizes at high temperatures, and this fact must be taken into account when it is considered for use. Its ability to withstand some reducing conditions is in its favor and is taken advantage of in some industrial applications when it is used as one leg of an iron-constantan thermocouple.

Some properties of constantan from references [43] and [72] are given in table 78.

TABLE 78. *Some properties of constantan*

Nominal specific resistance at 20 °C, 68 °F: 49 ohm cm × 10^{-6}, 294 ohms/cmf
Nominal temperature coefficient of resistance:
0.00001 (68–400 °F) per °F
±0.00002 (20–100 °C) per °C
Specific heat: 0.094 g cal/°C
Thermal conductivity at 100 °C: 0.0506 cal/sec/cm²/cm/°C
Nominal coefficient of linear expansion, (20–100 °C): 14.9 × 10^{-6} per °C
Tensile strength at 20 °C: maximum 100,000; minimum 60,000 psi
Density: 8.90 g/cm³; 0.322 lb/cu in.

Wise [90] gives curves of properties of commercial annealed alloys. Approximate values of some of the mechanical properties of constantan at presumably room temperature are: tensile strength 72,000 psi, elongation 48 percent, and elastic limit about 23,000 psi. Stauffer [91] points out that "the 55% copper-45% nickel has about the highest electrical resistivity, the lowest temperature coefficient of resistance, and the highest thermal emf against platinum of any alloys of these metals." The values of properties given by Stauffer agree very closely with those of table 78; and he gives, in addition, temperature coefficients of resistance over the ranges from 0 to 250 °C and 20 to 500 °C as 0 and ±0.000025 per degree C. He cites 500 °C as the maximum temperature of use of constantan in resistors and 900 °C as the upper limit for thermocouples.

The thermal emf of constantan is tailored to meet the use to which it is put, and so, a table of its thermal emf versus Pt 27 must be regarded as approximate. Table 79 gives the averages of the values obtained for seven samples by Corruccini and Shenker [73] and those obtained by Roeser and Dahl [63].

TABLE 79. *Thermal emf of constantan versus Pt 27*

Temperature	Reference [73]	Reference [63]	Temperature	Reference [73]	Reference [63]
°F	*emf, mv*	*emf, mv*	°F	*emf, mv*	*emf, mv*
32	0.00	0.00	1,000	−22.46	−22.55
100	−1.26	−1.27	1,100	−25.07	−25.15
200	−3.24	−3.26	1,200	−27.67	−27.77
300	−5.35	−5.39	1,300	−30.29	−30.39
400	−7.58	−7.64	1,400	−32.89	−32.99
500	−9.92	−9.98	1,500	−35.48	−35.58
600	−12.32	−12.40	1,600	−38.04	−38.14
700	−14.80	−14.88	1,700	−40.57	−40.66
800	−17.33	−17.41	1,800	−43.06	−43.13
900	−19.88	−19.97			

The variation with temperature of the resistivity of constantan (55 copper-45 nickel) as given by Roeser and Wensel [20] is presented in table 80.

TABLE 80. *Electrical resistivity of constantan* (55 Cu-45 Ni) *relative to the resistivity at 0 °C* (R_t/R_0)

The actual resistivity (ohms/cmf) is given for 0 °C.

Temperature		R_t/R_0	Temperature		R_t/R_0
°C	°F		°C	°F	
0	32	1.000	600	1,112	1.024
0	32	(294.2)	700	1,292	1.040
100	212	0.999	800	1,472	1.056
200	392	0.996	900	1,652	1.074
300	572	0.994	1,000	1,832	1.092
400	752	0.994	1,100	2,012	1.110
500	932	1.007			

2.3. Refractory Metals

The materials discussed in this section are generally the non-noble metals that can be used, alloyed or alone, to form thermocouples usable in the ranges above those covered by the current conventional thermocouples. The large amount of effort that has been and continues to be spent on the refractory metals is a direct result of the higher temperatures encountered in the jet, missile, and reactor technologies. The principal materials under investigation are the so-called refractory metals—tungsten, molybdenum, rhenium, tantalum, niobium, and their alloys. Iridium also has been considered for use in one leg of a high-temperature thermocouple, either alone or alloyed with one of the other metals mentioned.

Descriptions and properties of thermocouples of the refractory metals are found in the works of Sanders [93], Kuether [94], Lachman and Kuether [95], Kuether and Lachman [96], Lachman and McGurty [97], and of others as cited. The legs of the various thermocouples mentioned will be identified by the chemical symbols (tungsten W, molybdenum, Mo, etc.) in the discussion that follows, and temperatures will be reported as given; no corrections have been made to convert to the 1948 scale. Information on the refractory thermocouples will be presented along with properties of the wires, and the separation

TABLE 81. *Physical properties of tungsten*

Property	Unit	Condition	Values	
Mechanical properties				
Density	g/cm^3	Presintered at about 1,500 °C (2,700 °F)		10.0–13.0
		Sintered at up to 3,000 °C (5,400 °F)		16.5–17.5
		Swaged		18.0–19.0
		Drawn		19.0–19.3
Hardness	V.P.N	Sintered bar	200–250	
		Swaged bar	350–500	
		Cold rolled sheet	450–500	
		Recrystallized sheet	260–380	
Tensile strength and elongation	1,000 psi and percent	Sintered bar	18	------
		Swaged bar	50–213	------
		Wire 0.04 in. diam	256	1 to 4
		.02 in. diam	284	1 to 4
		.008 in. diam	355	1 to 4
		.004 in. diam	427	1 to 4
		.0008 in. diam	582	------
		Wire 0.004 in. diam, annealed (recryst.)	156	------
		Single crystal (containing Th)	156	20
Yield point	1,000 psi	Wire 0.02–0.04 in. diam		
		Annealed	99–113	
		Unannealed	213	
Hot tensile strength and corresponding elongation	1,000 psi and percent	Wire 0.025 in. diam		
		400 °C (750 °F)	170–227	2 to 3
		800 °C (1,470 °F)	113–142	4 to 5
		1,200 °C (2,200 °F)	57–85	5 to 6
		1,800 °C (3,270 °F)	14–42	
Young's modulus	psi × 10^{-6}	20 °C (70 °F)	59	
		1,000 °C (1,830 °F)	47	
Thermal properties				
Melting point	°C	3,410±20 (6,170 °F)		
Rate of evaporation	g/sq cm/sec	2,500 °C (4,530 °F)	7×10^{-8}	
		3,000 °C (5,430 °F)	2.4×10^{-5}	
Specific heat	cal/g °C	20 °C (70 °F)	0.033	
		1,000 °C (1,830 °F)	0.041	
		2,000 °C (3,630 °F)	0.047	
Thermal conductivity	cal/sec/cm^2/cm/°C	20 °C (70 °F)	0.31	
		1,000 °C (1,830 °F)	0.27	
		1,600 °C (2,910 °F)	0.25	
Linear coefficient of expansion	deg^{-1} C	20 °C (70 °F)	4.43×10^{-6}	
		1,000 °C (1,830 °F)	5.17×10^{-6}	
		2,000 °C (3,630 °F)	7.24×10^{-6}	
Electrical properties				
Specific resistance	microhm-cm	20 °C (70 °F)	5.5	
	ohms/cmf		33	
		1,000 °C (1,830 °F)	33	
			198	
		2,000 °C (3,630 °F)	66	
			397	
		3,000 °C (5,430 °F)	103	
			620	
Optical properties				
Total intensity of radiation	watts/sq cm	1,000 °C (1,830 °F)	2.5	
		2,000 °C (3,630 °F)	47	
		3,000 °C (5,430 °F)	240	

made previously between facts on thermocouple combinations and the separate elements will not be made.

The majority of the thermocouples proposed for use at the extreme upper temperatures for immersed sensors have tungsten for one leg. Because of its importance in this area, properties of tungsten are given in tables 81 and 82 in some detail from reference [101].

Similar information on molybdenum is given from reference [102] in tables 83 and 84. Information similar to that of tables 81 to 84 is found also in references [103], [104], and [105]. Other sources are available, but these cited, together with [101] and [102], were supplied in answer to a request circulated when this paper was contemplated, and supply most of the information required on tungsten and molybdenum.

The smallest diameter found in the trade literature for tungsten is 0.4 mil, and that for molybdenum is 1 mil. Larger sizes of wires and rods to any desired diameter are available.

From the chemical properties of tables 81 and 82, it is seen that at temperatures above 500 °C (932 °F) tungsten and molybdenum cannot be used in an oxidizing atmosphere and must therefore be protected if measurements are to be made under oxidizing conditions. No reaction between tungsten and nitrogen or hydrogen is said to occur at even the "highest temperatures," but molyb-

TABLE 82. *Chemical properties of tungsten*

Corrosive	Behavior
Hydrochloric acid, sulphuric acid, or nitric acid.	Cold, dilute or concentrated: practically insoluble Warm, dilute or concentrated: slight attack
Aqua regia	Cold: practically insoluble. Warm: rapid attack
Hydrofluoric acid	Cold or warm: insoluble
Hydrofluoric and nitric acid mixed	Rapid attack
Alkalies	Cold aqueous caustic soda or potash: practically insoluble. Molten caustic soda or potash or alkaline carbonates: a) in air: slow oxidation b) in the presence of oxidizing agents, e.g., KNO_3, KNO_2, $KClO_3$, PbO_2; rapid solution
Ammonia	Practically insoluble to attack by aqueous solution, slight attack in the presence of H_2O_2
Sodium nitrite	Molten: rapid solution above 300 °C (570 °F)
Carbon (lampblack, graphite, charcoal) and hydrocarbons	Formation of carbides from 1,400 °C (2,550 °F), complete carburization to WC at 1,400 to 1,600 °C (2,550 to 2,900 °F)
Sulphur	Molten or boiling: slow attack
Mercury and mercury vapor	Practically insoluble
Aluminum oxide, magnesium oxide.	Reduction to metal in contact with tungsten above 1,900 °C (3,450 °F)
Thorium oxide	Reduction to metal in contact with tungsten above 2,200 °C (4,000 °F)
Air and oxygen	Insoluble at room temperature; oxidation starts from 400 to 500 °C (750 to 930 °F); at temperatures above this rapid oxidation to WO_3 and vaporization
Water	Insoluble at all temperatures
Water vapor	At red heat rapid oxidation to WO_3
Hydrogen	No reaction up to melting point
Nitrogen	No reaction up to highest temperatures
Ammonia	Slight formation of nitrides with powder from 700 °C (1,290 °F). Nitrides dissociate above this temperature
Carbon monoxide	Carburization begins at 800 °C (1,470 °F)
Carbon dioxide	Oxidation above 1,200 °C (2,190 °F)
Halogens	Fluorine: attack at normal temperatures Chlorine: attack at 250 °C (480 °F) Bromine and iodine: attack at light red heat
Hydrogen chloride gas	Up to 600 °C (1,110 °F) no attack if free of oxygen
Nitric oxide	Oxidation to WO_2 at high temperatures
Hydrogen sulphide	Surface attack at red heat
Sulphur dioxide	Oxidation at high temperatures
Carbon disulphide	Attack at red heat

TABLE 83. *Physical properties of molybdenum*

Property	Unit	Condition	Values
Mechanical data			
Density	g/cm^3	Pressed, unsintered	6.1 to 6.3
		Sintered	9.2 to 9.4
		Swaged	10.0 to 10.28
Hardness	Vickers (kg/sq mm)	Sintered bar	150 to 160
		Swaged bar	200 to 230
		Annealed sheet	250 to 300
Tensile strength and elongation	1,000 psi and percent	Drawn wire:	
		1 mm (0.04 in.) diam	142 to 200 1 to 3
		0.05 mm (0.002 in.) diam	312 to 355 1 to 3
		Annealed wire:	
		1 mm (0.04 in.) diam	114 to 142 10 to 15
		0.03 mm (0.0012 in.) diam	114 to 170 10 to 20
		Single crystal	~50 ~30
Yield point	1,000 psi	Unannealed wire: 0.1 to 0.5 mm (0.004 to 0.02 in.) diam.	80 to 90 percent of the tensile strength.
Hot tensile strength	1,000 psi and percent	Wire 0.6 mm (0.024 in.) diam:	
		200 °C (390 °F)	114 to 142 4 to 5
		400 °C (750 °F)	85 to 100 4 to 5
		800 °C (1470 °F)	71 to 85 4 to 5
		1200 °C (2,190 °F)	28 to 43 5 to 6
Modulus of elasticity	1,000 psi		47,800
Thermal properties			
Melting point	°C (°F)	2,630±40 (4,740±72 °F)	
Vapor pressure	mm Hg	1,500 °C (2,730 °F)	6.4×10^{-9}
		1,800 °C (3,270 °F)	8.0×10^{-7}
		2,000 °C (3,630 °F)	4.15×10^{-5}
Specific heat	cal/g °C	20 °C (68 °F)	0.065
		1,000 °C (1,830 °F)	0.075
		1,400 °C (2,550 °F)	0.080
Thermal conductivity	cal/sec/cm²/cm/°C	20 °C (68 °F)	0.37
		1,000 °C (1,830 °F)	0.25
		1,600 °C (2,910 °F)	0.16
Linear coeff. of expansion	$deg^{-1}C$	20 °C (68 °F)	5.3×10^{-6}
Electrical properties			
Resistivity	microhm-cm ohms/cmf.	20° C (68 °F)	5 30
		1,000 °C (1,830 °F)	27 162
		1,500 °C (2,730 °F)	43 259
		2,000 °C (3,630 °F)	60 361

TABLE 84. *Chemical properties of molybdenum*

Reagent	Behavior
Hydrochloric acid, sulphuric acid.	Cold, dilute or concentrated: practically resistant Warm, dilute or concentrated: slight attack
Nitric acid and aqua regia	Cold, concentrated: slow attack Cold, dilute: more rapid attack Warm, dilute or concentrated: severe attack and complete solution
Hydrofluoric acid	Cold or warm: no reaction
Hydrofluoric acid-nitric acid mixtures.	Severe attack, rapid solution
Alkalies	Cold aqueous caustic soda or potash: practically resistant. Fused caustic soda or potash or alkaline carbonates: a) in air: slow oxidation b) in the presence of oxidizing agents such as KNO_3, KNO_2, $KClO_3$, PbO_2: violent reaction, solution
Fused oxidizing salts (KNO_3 KNO_2 Na_2O_2 $KClO_3$).	Violent reaction, solution
Ammonia	Aqueous solution: slow attack Gas: resistant up to red heat
Carbon (lampblack, graphite or charcoal).	Surface carburized above 1,100 °C (2,010 °F), completely carburized above 1,300 to 1,400 °C (2,370 to 2,550 °F)
Sulphur	No reaction up to 440 °C (825 °F), sulphides form at higher temperatures
Mercury liquid and vapor	Completely resistant
Phosphorus	No reaction even at high temperatures
Boron	Borides form at high temperatures
Silicon	Silicides form at high temperatures
ZrO_2, MgO, Al_2O_3, magnesite, chrome magnesite.	The metal reacts with the pure oxides above 1,600 °C (2,900 °F)
Air or oxygen	Practically no reaction at room temperature. Oxidation above 400 °C (750 °F). Rapid oxidation to MoO_3 above 600 °C (1,110 °F) and sublimation
Steam	Rapid oxidation at red heat
Hydrogen	No reaction below melting point
Nitrogen	No reaction up to 2,400 °C (4,350 °F), formation of nitrides at higher temperatures
Nitrogen-hydrogen (cracked ammonia).	No reaction
Nitrous oxide and nitric oxide	Oxidation to MoO_3 at red heat
Carbon dioxide	Oxidation above 1,000 °C (1,830 °F)
Carbon monoxide	Carburized above 1,000 °C (1,830 °F)
Hydrocarbons	Carburized above 1,000 °C (1,830 °F)
Halogens	Fluorine: reaction at room temperature. Chlorine and bromine: attack at red heat. Iodine: no reaction even when hot
Hydrogen sulphide	Formation of sulphide at 1,200 °C (2,190 °F)
Sulphur dioxide	Oxidation at red heat

denum forms a nitride at temperatures above 2,400 °C (4,352 °F). There is no reaction with hydrogen. The choice of atmosphere in a protection tube containing these materials thus must be made with care from the standpoints of both the effect of the atmosphere on the thermocouple materials and the effect on the insulating refractory.

In connection with the refractories usable in the temperature regions where these materials find application; aluminum oxide and magnesium oxide are said to suffer a reduction to metal in contact with tungsten above 1,900 °C (3,452 °F), and thorium oxide is similarly affected at temperatures above 2,200 °C (3.992 °F). Molybdenum is said to react with pure zirconium, magnesium, and aluminum oxides at temperatures above 1,600 °C (2,912 °F). Here again caution must be exercised to select materials that are compatible.

The W–Mo thermocouple appears to have been used in early attempts to make practical sensors of the refractory metals. It has been used successfully in molten steel and still appears to find favor in some areas. One reason for its acceptance seems to be its ability to withstand reducing atmospheres, in spite of its sensitivity to some of the gases listed in tables 82 and 84. Its disadvantages have been its brittleness, instability in use, lack of thermoelectric reproducibility, low thermal emf, and a polarity reversal at about 1,250 °C (2,282 °F). Improvement has been achieved in some of these properties but the undesirable thermoelectric features remain. The temperature-emf relationship for the W versus Mo thermocouple from 0 °C (32 °F) to 2,200 °C (3,992 °F), as calculated from the equations of reference [106], is given in table 85, and approximate values have been taken from the curve of reference [97].

TABLE 85. *Thermal emf of the tungsten versus molybdenum thermocouple*

a. Reference[106]

Temperature		Emf	Temperature		Emf
°C	°F	mv	°C	°F	mv
0	32	0	1,200	2,192	−0.98
200	392	−0.85	1,400	2,552	+0.06
400	752	−1.14	1,600	2,912	1.42
600	1,112	−1.36	1,800	3,272	2.88
800	1.472	−1.54	2,000	3,632	4.10
1,000	1,832	−1.46	2,200	3,992	4.94

b. Reference [97]

Temperature	Emf	Temperature	Emf
°F	mv	°F	mv
32	0	2,400	−0.22
400	−1.00	2,800	+1.30
800	−1.70	3,200	+2.95
1,200	−1.99	3,600	+4.60
1,600	−1.81	4,000	+6.38
2,000	−1.23		

The emf of the W versus Mo thermocouple derived from the Battelle equations [106] for W versus Re and Mo versus Re is lower than that found generally, even though the Battelle data for these two thermocouples are in reasonable agreement with those of most other investigators. On the whole, the data of Lachman and McGurty [97] seem to be more nearly representative of most of the calibrations found of the W versus Mo thermocouple.

The approximate upper temperature limit for the W versus Mo thermocouple is given in reference [107] as 2,400 °C (4,352 °F), which is more than 200 °C below the melting point of molybdenum (see table 83).

Rhenium until recently appears to have been largely a scarce curiosity with little practical use. According to reference [109], however, "Extensive work has recently been reported on the metal rhenium, both in this country and abroad [110, 111]. Rhenium is a strong, ductile, refractory metal with a melting point of 3,180 °C (5,756 °F). It has a high electrical resistivity, hexagonal close-packed crystal structure, and some chemical and metallurgical properties characteristic of the precious metals. In England, extremely interesting exploratory work on tungsten- and molybdenum-base alloys containing about 35 atomic percent rhenium has shown these materials to

have exceptional ductility [112]." Rhenium thus appears to have desirable properties itself, and also to have the capability of imparting these properties to its alloys with tungsten and with molybdenum. Thermocouples of tungsten and rhenium, and of alloys of tungsten and rhenium appear to be gaining favor, and it seems probable that one of these thermocouples will be selected for most general use at the upper temperatures as an immersed sensor. Some properties of unalloyed rhenium follow.

Indications of the purity of available metal are seen in table 86 of analyses of rhenium used in the work of reference [106]. Analyses of tungsten and molybdenum are included.

TABLE 86. *Analyses of rhenium, molybdenum, and tungsten*

[Impurity content,[a] weight percent]

Element	Rhenium		Molybdenum	Tungsten
	Powder	Strip	Powder	Powder
Al	<0.01	0.010	----------	<0.001
C	----------	----------	0.012	.002
Ca	<0.01	----------	.005	<.001
Cr	ND	----------	.002	<.001
Cu	<0.01	----------	----------	<.001
Fe	0.0008	0.005	0.002	<.001
K	ND	----------	----------	.001
Mg	<0.010	0.005	0.001	<.001
Mn	----------	----------	----------	<.001
Mo	ND	0.005	----------	.004
Na	ND	----------	----------	<.001
Ni	ND	----------	0.005	<.001
O	----------	----------	.010	.031
Si	<0.01	0.007	<.01	<.001
W	----------	----------	<.01	----------

[a] ND designates not detected in spectrographic analysis.

Impurities in the rhenium are seen to total about 0.05 percent or less. No statement of homogeneity of rhenium wire is available, but according to reference [106] "good reproducibility from run to run (of W versus Re and Mo versus Re combinations) was obtained, and the average curves (thermal emf) obtained were in excellent agreement with the data obtained from other laboratories."

Some mechanical properties of rhenium sheet are given in table 87 [108].

TABLE 87. *Tensile and elongation data for annealed and cold-rolled rhenium sheet*

	Annealed	Reduced 12.9%	Reduced 24.7%	Reduced 30.7%
Rolled thickness---------mils--	10.1	8.8	7.6	7.0
Proportional limit---------psi--	31,700	25,200	42,200	159,000
0.1 percent offset yield strength--psi--	131,000	233,000	279,000	282,000
0.2 percent offset yield strength--psi--	135,000	245,000	298,000	311,000
Ultimate tensile strength---------psi--	168,000	250,000	307,000	322,000
Elongation in 1 in---------percent--	28	8	2	2
Reduction of area---------percent--	30	24	1	1

Rhenium wire containing 0.5 percent thoria prepared for electronic studies [108] was drawn down to a diameter of 2.9 mils. Below a diameter of 15 mils, two 10 percent reductions could be taken between anneals, and the authors believe that finer sizes could be prepared. No annealing temperature is given for this particular operation, but elsewhere annealing at temperatures of 1,700 °C (3,092 °F) and 1,800 °C (3,272 °F) for periods up to 2 hrs is mentioned.

The modulus of elasticity of rhenium varies almost linearly from about 67.5×10^6 psi at room temperature to 54×10^6 psi at 880 °C (1,616 °F).

The electrical resistivity of rhenium containing copper, tin, aluminum, silicon, magnesium, calcium, and molybdenum to a total of 0.0585 percent and gold given as 0.0X percent is given in table 88.

TABLE 88. *Electrical resistivity of rhenium from 20 to 2,400 °C*

Temperature		Resistivity	Temperature		Resistivity
°C	°F	*ohms/cmf*	°C	°F	*ohms/cmf*
20	68	116	1,400	2,552	541
200	392	197	1,600	2,912	578
400	752	280	1,800	3,272	608
600	1,112	349	2,000	3,632	632
800	1,472	403	2,200	3,992	650
1,000	1,832	460	2,400	4,352	662
1,200	2,192	505			

Approximate values of the specific heat of rhenium, taken from a curve of reference [108], are given in table 89. The discontinuity at 1,500 °K is a result of extension of the determinations upward in the work of reference [108] from the earlier determinations of Jaeger and Rosenbohm [110] that covered the temperature range up to only 1,473 °K.

TABLE 89. *Specific heat of rhenium*

Temperature	Specific heat	Temperature	Specific heat
°K	*cal/g °K*	°K	*cal/g °K*
300	0.0325	1,800	0.0432
600	0.0348	2,100	0.0457
900	0.0367	2,400	0.0483
1,200	0.0383	2,700	0.0503
1,500	0.0400	----------	----------

The density of rhenium, from reference [110], is 21.04 g/cm^3.

The linear thermal expansion of rhenium containing about 0.2 percent impurities, from reference [110], is given in table 90.

TABLE 90. *Linear thermal expansion of rhenium*

Temperature		l_t/l_{20} °C	Temperature		l_t/l_{20} °C
°C	°F		°C	°F	
20	68	1.00000	600	1,112	1.00396
100	212	1.00066	700	1,292	1.00462
200	392	1.00132	800	1,472	1.00528
300	572	1.00198	900	1,652	1.00594
400	752	1.00264	1,000	1,832	1.00660
500	932	1.00330	----------	----------	----------

No information on the thermal conductivity of rhenium seems to be available for temperatures above about 175 °K.

The spectral emissivity of rhenium, attributed in reference [113] to D. T. F. Marple, is given for two temperatures in table 91.

TABLE 91. *Spectral emissivity of rhenium*

Temperature	Emissivity, percent at wavelength (microns) of								
	0.3	0.4	0.6	0.8	1.2	1.6	2.0	2.4	2.8
°R									
3,560	42.5	42.5	41.0	39.0	32.5	27.5	25.0	22.5	22.0
5,480	42.5	42.5	41.0	39.0	34.0	30.5	28.5	27.0	25.5

TABLE 92. *Thermal emfs of* W *versus* Re *and* Mo *versus* Re *thermocouples* [106]

Temperature		Emf		Temperature		Emf	
		W-Re	Mo-Re			W-Re	Mo-Re
°C	°F	mv	mv	°C	°F	mv	mv
0	32	0	0	1,200	2,192	18.94	19.92
100	212	0.55	1.10	1,300	2,372	20.65	21.15
200	392	1.59	2.44	1,400	2,552	22.22	22.16
300	572	2.96	3.98	1,500	2,732	23.66	22.95
400	752	4.55	5.69	1,600	2,912	24.96	23.54
500	932	6.27	7.52	1,700	3,092	26.09	23.93
600	1,112	8.06	9.43	1,800	3,272	27.05	24.18
700	1,292	9.90	11.37	1,900	3,452	27.86	24.33
800	1,472	11.75	13.29	2,000	3,632	28.56	24.46
900	1,652	13.60	15.14	2,100	3,812	29.15	24.66
1,000	1,832	15.43	16.89	2,200	3,992	30.00	25.05
1,100	2,012	17.23	18.49				

The variation of emissivity at 0.665μ with temperature, credited in reference [113] to Sims, Craighead, Jaffe, et al., shows in one case that the emissivity is constant at 40 percent over the range from 500 to 5,500 °R. In another set of determinations the emissivity is about 43.5 percent at 500 °R, remains practically constant up to about 1,700°, and drops off to about 42 percent at 3,000 °R. From here it decreases almost linearly to about 37 percent at 5,000 °R and somewhat more slowly to a little over 36 percent at 5,500 °R.

The temperature-emf relationships for the W versus Re and Mo versus Re thermocouples, as calculated from the equations of reference [106], are given in table 92. Data for the same thermocouples, from reference [122], are given in table 93.

The thermoelectric powers of both thermocouples are seen to decrease in the upper part of the range. (The apparent increase between 2,100 and 2,200 °C in the table is as calculated, but is not confirmed experimentally.) Various combinations of tungsten and tungsten-rhenium alloys have been investigated in attempts to find sensors that do not exhibit the flattening of the thermal emf versus temperature relationship that limits the usefulness of the W versus Re and Mo versus Re thermocouples. Results of work on these materials, taken directly from reference [97], are presented in table 94.

Compositions of the thermocouple materials used in the work of Lachman and McGurty, taken from reference [97], are given in table 95.

TABLE 93. *Thermal emfs of* W *versus* Re *and* Mo *versus* Re *thermocouples* [122]

Temperature	Emf		Temperature	Emf	
	W-Re	Mo-Re		W-Re	Mo-Re
°F	mv	mv	°F	mv	mv
32	0	0	2,200	18.99	18.59
200	0.70	1.00	2,400	20.72	19.70
400	1.91	2.60	2,600	22.38	20.67
600	3.47	4.45	2,800	23.96	21.89
800	5.24	6.44	3,000	25.41	22.23
1,000	7.15	8.42	3,200	26.64	----------
1,200	9.19	10.41	3,400	27.58	----------
1,400	11.22	12.31	3,600	28.32	----------
1,600	13.26	14.12	3,800	28.92	----------
1,800	15.24	15.76	4,000	29.21	----------
2,000	17.17	17.26			

TABLE 94. *Calibration data for tungsten versus rhenium-alloy thermocouples, and for thermocouples of two tungsten-rhenium alloys*

Temperature		W/W-20% Re	W/W-26% Re	W-3% Re/W-20% Re	W-5% Re/W-26% Re
°C	°F	emf, mv	emf, mv	emf, mv	emf, mv
93	200	0.143	0.310	0.763	1.139
204	400	0.634	1.110	2.040	2.864
316	600	1.460	2.152	3.546	4.596
427	800	2.625	3.660	5.215	6.682
538	1,000	3.989	5.482	6.830	8.760
649	1,200	5.530	7.450	8.565	10.888
760	1,400	7.248	9.395	10.255	12.988
871	1,600	9.009	11.601	11.980	14.992
982	1,800	10.875	14.030	13.710	16.939
1,093	2,000	12.690	16.535	15.420	18.860
1,204	2,200	14.555	19.052	17.075	20.716
1,316	2,400	16.260	21.395	18.660	22.484
1,427	2,600	18.010	23.705	20.290	24.235
1,538	2,800	19.795	25.675	21.810	25.898
1,649	3,000	21.50	27.87	23.29	27.63
1,760	3,200	23.23	30.14	24.68	29.13
1,871	3,400	24.97	32.28	26.16	30.58
1,982	3,600	26.60	34.20	27.28	32.13
2,093	3,800	28.12	36.12	28.58	33.21
2,204	4,000	29.75	37.83	29.71	34.40
2,316	4,200	31.05	39.64	30.77	35.49
2,427	4,400	32.20	41.25	31.69	36.42
2,538	4,600	33.45	42.56	32.61	37.31
2,649	4,800	34.65	43.99	33.55	38.00
2,760	5,000	35.60	44.79	34.38	38.45
2,871	5,200	36.50	----------	35.15	----------

TABLE 95. *Chemical analyses of tungsten-rhenium alloys and tungsten, from reference* [97]

Composition	Chemical analysis											
	W	Re	Mo	Fe	Cu	Al	Si	Mg	Ni	O_2	C	S
	wt %	wt %	wt %	wt %	wt %	wt %	wt %	wt %	wt %	wt %	ppm	ppm
W-1% Re	98.12	1.22	0.005	0.003	0.001	0.01	----------	----------	----------	0.123	186	<10
W-3% Re	96.26	3.24	.005	.002	.001	.006	----------	----------	----------	.048	138	<10
W-5% Re	93.98	5.35	.004	.004	.002	.001	----------	----------	----------	.079	211	<10
W-10% Re	89.68	9.98	.005	.005	.001	----------	0.001	0.001	----------	----------	----------	----------
W-20% Re	82.22	17.21	.005	.005	.002	.002	----------	----------	----------	.044	173	<10
W-26% Re	75.32	23.85	.04	.01	----------	.004	.003	----------	0.004	.133	390	<10
Tungsten	----------	----------	<.001	.001	<.001	.001	<.001	<.005	.005	.010	75	----------

From the data of table 94 it appears that the W versus W-Re 26 percent thermocouple is the optimum from the standpoints of thermoelectric power and near-linearity up to about 5,000° F. Some anomalies are seen in each of the calibrations that could cause complications in the use of any of these thermocouples. The reasons for these irregularities is not known; they may be definite properties of the thermocouples, or they may be a consequence of the difficulties inherent in calibrating at the high temperatures covered. The conclusion of Lachman and McGurty [97] on their work on rhenium alloys in thermocouples is ". . . the tungsten/tungsten-26 percent rhenium thermocouple offers a vast improvement over the pure tungsten/rhenium type so far as high temperature capabilities (in the 5,000 °F range) and accuracy are concerned."

Tantalum has been considered for use in thermocouples, either unalloyed or alloyed. It does, however, in the unalloyed form exhibit some irregularities in its behavior above 1,200 °C when coupled with rhenium, or with any other material that gives a smooth temperature-emf relationship with rhenium. According to Steven, page 363 of reference, [107] "The metals tantalum and niobium fell by the wayside because of their great affinity for residual gas molecules at elevated temperatures and the shift in electromotive calibration resulting from this 'getter' action." Some properties of tantalum along with those of other refractory metals are given by Steven in the same reference.

The tungsten versus iridium thermocouple [99] gives a smooth and probably the most nearly linear temperature-emf relationship of any of the high-temperature thermocouples. One of its obvious advantages is its high thermoelectric output, but because of the iridium leg, its use is limited to a maximum temperature of about 2,200 °C (3,992 °F). Although iridium is more resistant to oxidizing conditions than is tungsten, it does not survive long exposure near the upper useful limit. Unlike tungsten, it is not at its best under some reducing conditions, and so caution should be exercised that the uses to which the tungsten versus iridium thermocouple is put are compatible with good service.

Troy and Steven [99] give the thermoelectric power of this thermocouple as 22.9 μv per degree at 1,000 °C, 25.0 at 1,600 °C, and 26.3 μv per degree at 2,000 °C. Their calibration is given in table 96.

TABLE 96. *Thermal emf of the tungsten versus iridium thermocouple*

Temperature		Emf	Temperature		Emf
°C	°F	mv	°C	°F	mv
1,000	1,832	14.25	1,600	2,912	28.62
1,100	2,012	16.56	1,700	3,092	31.12
1,200	2,192	18.91	1,800	3,272	33.69
1,300	2,372	21.3	1,900	3,452	36.28
1,400	2,552	23.70	2,000	3,632	38.88
1,500	2,732	26.15			

2.4. Carbon and Carbides

Carbon and carbides for many years have been subjects of investigations to avoid problems inherent in the use at high temperatures of thermocouples of metals and alloys. Thermocouples of this kind have not yet, from the number in use, assumed an important position in the temperature measuring field; but some are used now, and the possibility exists that more will be used in the near future. Only a brief mention of the several types of these thermocouples is made here; the information has been taken chiefly from reference [114].

According to Thielke and Shepard [114] they have had little success with graphite versus carbon thermocouples. Their sensor of this type started off at room temperature with a thermoelectric power of 8 μv per degree C (4.4 μv/°F), and reached a maximum thermal emf of 7 mv at 1,600 °C. They do, however, mention the work of Ubbelhode, Blackman and Dundas [115], who have reported a thermocouple based on the difference in thermoelectric power betwcen graphite of different crystal orientation. The following quotation is from reference [114].

"They report work on single crystals of graphite where the limiting value of thermoelectric power in the *a*-axis direction is about -3 μv/°C and the limiting value in the *c*-axis direction is $+1.86$ μv/°C at 20 °C. They (Ubblehode, et al.) formed a couple from materials having the greatest practical difference in orientation, one element being a pyrolytic filament and the other (evidently) a pressed natural graphite. The couple has an output of about 35 mv at 2,400 °C, with a sensitivity at room temperature of about 25 μv/°C. This is too great to be accounted for by the algebraic sum of the *a*-axis and *c*-axis thermoelectric powers (about 5 μv/°C), but as they note, 'the thermoelectric power of various specimens . . . depends on various defects in the carbon networks in graphite, as well as on the crystal orientations'. Even though the interpretation of the nature of the couple may be difficult, its output is substantial and its value as an instrument is very appealing."

Another approach to the effect of crystalline perfection was, according to Thielke and Shepard based on the work of Bidwell [116]. The effect of baking temperature on the thermoelectric power of graphite was determined, and it was found that one rod baked to 2,000 °C (3,632 °F) and an identical rod baked to 3,000 °C (5,432 °F) produced an output of 25 mv at 1,000 °C (1,832 °F) that was linear from about 200 °C (392 °F) to 1000 °C. They say that this thermocouple might be useful up to 2000 °C, but that use above this temperature would alter the characteristics of the rod baked at 2,000 °C and thus the calibration of the thermocouple.

The most successful combination of carbon with metals is said in reference [114] to be that of tungsten and graphite, described by Watson and Abrams [117], who gave a calibration of this thermocouple to 1,600 °C (2,912 °F) and reported the favorable use of it to 2,400 °C (4,352 °F) in a reducing atmosphere and repeated use in vacuum at 1,850 °C (3,352 °F). Stevens points out in

reference [20], pp. 357–376, that this thermocouple is sensitive to moisture content in the graphite leg, but that the calibration can be restored by baking. The maximum emf is reported as 45 mv at 2,100 °C (3,812 °F), although the upper temperature is said to be 2,400 °C (4,352 °F).

The carbon vs silicon carbide thermocouple announced by Fitterer in 1933 [118, 119] had an output of 508 mv at 1,700 °C (3,092 °F) with, according to reference [114], possible use up to 2,700 °C (4,892 °F). The maximum thermoelectric power was about 300 μv per degree C (167 μv/°F), a colossal figure when compared with outputs of conventional thermocouples. Fitterer also reported on thermocouples of C and MoC giving an output of 16 mv at 1,050 °C (1,922 °F), and on one of C versus WC that gave an output of 10.5 mv at 860 °C (1,580 °F). Ridgway [120] received a patent in 1939 on a thermocouple of B_4C and C having an output of 600 mv at 2,400 °C, which is comparable to that of the C versus SiC thermocouple of Fitterer. Its thermoelectric power is 330 μv per degree C (184 μv/°F) over the range 500° to 1,700 °C.

Graphite versus doped graphite thermocouples, have, according to Thielke and Shepard [114], been used successfully and appear to have possibilities of continued and expanded applications. The doped element which they describe contains about 1 percent boron in graphite [120]. This thermocouple was calibrated to 3,100 °C (5,612 °F) and showed "a continuously increasing output to that temperature with an output of about 90 millivolts at 2000 °C (3,632 °F) and a sensitivity of 50 microvolts per °C (28μv/°F) between 500° and 1,200 °C (932° and 2,192 °F) . . . ." The same authors also say that "the choice of a heavily doped boron-graphite element is based on two considerations: first, small losses of boron from a heavily doped element have little effect on the room temperature thermoelectric power of the graphite; second, the thermoelectric power of the heavily doped graphite maintains a high value at high temperatures, whereas the value for low concentrations of boron drops off with increasing temperature."

The behavior of the graphite versus boron-doped graphite thermocouple from field tests has shown, according to reference [114]:

"(a) Stable operation of the boron/graphite couples in a vacuum crystal growing furnace for at least 300 hr at 1,400 °C, compared to a maximum of 36 hr using Pt/Pt-Rh.

"(b) Continuous operation of the couples in a refractory-producing furnace operating at 1,800° to 1,900 °C.

"(c) Use of the couples in a high pressure crystal growing furnace with no failure after 60 heating cycles of 6 hr each to temperatures between 1,500° and 2,000 °C.

"(d) Successful use of the couples as immersion pyrometers for steel melts, providing accuracy to within 10 °C and response times as low as four seconds."

The usefulness of all of the thermocouples of carbon and carbides has been limited by the bulkiness, fragility, and questionable reproducibility. The possibility that fabrication of carbides may be developed to the point where reproducibility is improved is visioned in reference [114], and small thermocouples of graphite and boron-doped graphite are mentioned. In addition, pyrolytic filaments of 0.020-in. and 0.0008-in. diameters have been treated to form graphite vs. doped graphite thermocouples. Further, the development of graphite cloth and yarn at the National Carbon Company is said to provide material from which these thermocouples can be made in flexible form. It appears that by these latter two means flexible thermocouples can be made that will give fast response and freedom from the limitations imposed by the use of the bulky, fragile, larger thermocouples of this kind that have been considered.

Properties of various carbon and carbide thermocouples are summarized in table 97, taken from reference [114].

TABLE 97. *Thermocouples using carbon and its modifications*

Couple	Maximum temperature	Maximum emf	Maximum sensitivity	Notes—accuracy, interchangeability, resistance
	°C	mv	μv/°C	
W/Gr	2,400	45(2,100 °C)	29(800 °C)	½ ohm; ±10 °C below 1,600°; 5 percent interchangeability.
	1,623	36.22(1,623 °C)	22(1,500–1,700 °C)	
C/Ni	1,250			
C/Gr	2,000	0.049(1,900 °C)	0.02	±50 °C
	1,400	0.04(1,400 °C)		
	2,400	7(1,600 °C)	8(700–1,000 °C)	
Gr/Gr (BT)	1,900	36(1,900 °C)	27 ½(300–1,000 °C)	2,000° baked stock versus 3,000° baked; ±10 °C accuracy
Gr/Gr (*a.* versus *c.*)	2,500	34(2,300 °C)	20(400 °C)	*c*-axis graphite versus *a*-axis graphite; ±20 °C
BGr/Gr	2,600	112(2,700 °C)	62(900 °C)	±10° accuracy; ±35° interchangeability; ½ ohm resistance
B_4C/C	2,400	650(2,400 °C)	330(500–1,700 °C)	
Gr/SiC	2,700	508(1,700 °C)	300(1,200–1,700 °C)	5 ohm; ±10 °C accuracy; 1 percent interchangeability
Gr/MoC	1,050	16(1,050 °C)	16(300–1,100 °C)	
Gr/WC	850	10 ½(850 °C)	16(400–900 °C)	

3. Ceramic-Packed Thermocouple Stock[6]

The ceramic-packed thermocouples discussed here comprise thermocouple wires packed tightly in ceramic insulating material enclosed in a metal tube. This means of insulation for use at high temperatures has been used for a long time in resistance heating elements, but it is only since the arrival on the scene of jet engines and gas turbines that it has been applied so widely to thermocouples. Although initial applications were in the turbine-type engines, the versatility and other desirable properties of the thermocouples are so attractive that they now are accepted throughout industry and technology. The purpose here is, because of the widespread interest in this type of thermocouple stock, to point out briefly some of its properties that are of interest in applications.

The general versatility of the ceramic-packed wire is described in catalogs of some suppliers of this material. When quotations are given here from such sources the phrase "ceramic-packed" is substituted for brand or company names. One statement [121] on the versatility of this material follows.

> "The characteristics of ceramic-packed wire make it ideal for a wide variety of applications. Flexibility is one of these highly desirable qualities; ceramic-packed wire can be formed to a radius equal to the sheath diameter without loss of insulation. It will fit any contour, yet remain rigid after bending; it can be cut to short lengths and connectors attached. It may be imbedded in concrete, plaster, or similar materials or buried underground."

No mention is made in this statement about the rigorous conditions under which the packed stock must and does perform when it is subjected to the temperatures, vibrations, and atmospheres encountered in aircraft engine use.

3.1. Thermocouple Wires

All of the conventional thermocouple wires are available in the ceramic-packed stock, and some makers indicate that they will supply any suitable wires in such material. The most popular thermocouples so mounted today are, however, the type K and iron versus constantan. The range of wire sizes found in catalogs is from a diameter of about 0.001 in. to B & S 12-gage (0.081 in.). Stock containing one or two wires is generally available, and some with multiple wires are in the catalogs.

Several types of measuring junctions are available. The most common types of bare measuring junctions are the V, the U, the loop, and variations of these to meet special requirements. Totally enclosed junctions that protect the wires from physical or chemical damage fall generally into two styles, one in which the thermocouple is grounded to the closed end of the sheath, and the other in which it is not grounded. Another enclosed-junction type [123, 124] that uses single-wire stock provides a butt-welded measuring junction in a continuous unwelded sheath. This type assembly can be used as a straight-through probe or can be formed into a loop.

Another type of junction that is used more in special applications is one in which a thin metallic film is used to form a surface junction across the square-cut end of coaxial stock. [125] The sheath serves in this type as one leg of the thermocouple, and the single, coaxial wire serves as the other. The metallic film is vacuum deposited to a thickness of about one micron. One of the advantages claimed for this type of junction is fast response to a temperature change.

Additional types, mentioned in reference, [124] are the differential and the pencil or tapered in which the closed end at the measuring junction is tapered like a pencil point to give less mass and consequent faster response to a temperature change.

Various types of connections and connecting heads are available, but these are outside of the scope of this paper and are not discussed here.

Makers of the sheathed stock normally claim that the limits of error for the thermocouple types listed in reference [1] are within the ISA tolerances, and in most cases give their own estimates of limits of error for thermocouples not listed in reference [1]. The types listed by ISA are often said to be carried in stock, and the less common thermocouples are made up on order.

The ceramic-packed stock is available in outer diameters ranging from 0.010 in. to about ½ in. The recommended minimum radius of bending differs among the suppliers, but the range found is from one to four diameters. Some makers suggest that the stock be heated to make the sharper bends.

Information from three suppliers [124,126,121] on dimensions and wire sizes of available stock is given in table 98. The first two tables are presumably for two-wire stock and the third is for stock with up to four wires.

Inconel and stainless steels seem to be the most popular sheath materials, but a large assortment is offered by the various makers. A composite list of the various materials said to be available from several makers is given in table 99 together with some properties. Some of the information is from reference [126], and advantage has been taken of the thorough survey by Anderson and MacKenzie [127] for the most of the remainder of the data given. Values from the latter work are chiefly scaled from charts, and so must be considered approximate.

[6] Most of the information available on the ceramic-packed stock is from catalog or advertising literature, and consequently practically all given here is from such sources. No implication is intended that materials from industrial organizations whose literature is cited are superior to those of others, and no endorsement of any product over any other is implied herein.

TABLE 98. *Dimensions and wire sizes of available ceramic-packed stock*

(a)

Sheath diameter	Standard wire	Maximum wire	Maxium length
in.	*B & S gage*	*B & S gage*	*ft*
0.010	50	46	25
.020	38	38	150
.025	36	34	150
.032	35	34	150
.040	34	32	200
.062	29	28	200
.091	26	26	100
.114	25	25	100
.125	24	22	100
.187	20	18	60
.250	18	16	60
.312	16	14	60
.375	14	14	40
.437	14	12	40
.500	12	12	25

(b)

Sheath outside diameter	Outside diameter tolerance	Nominal wall thickness	Approximate wire	Maximum length
in.	±*in.*	*in.*	*B & S gage*	*ft*
0.020	0.001	0.003	38	250
.032	.001	.005	36	250
.040	.001	.007	34	250
.062	.002	.010	29	150
.090	.002	.014	26	125
.125	.002	.018	24	100
.188	.003	.025	18	60
.250	.003	.032	17	40
.313	.003	.040	16	40
.375	.003	.049	14	30
.430	.003	.065	13	30
.500	.003	.065	12	30

(c)

Sheath diameter	Sheath wall thickness	Nominal conductor diameters			
		1-wire	2-wire	3-wire	4-wire
in.	*in.*	*in.*	*in.*	*in.*	*in.*
0.313	----	0.064	0.051	0.040	0.040
.250	----	.051	.040	.032	.032
.188	----	.040	.032	.022	.022
.125	0.014	.032	.022	.011	.011
.062	.010	.022	.011	.006	.006
.040	.007	.011	.006	----	----
.025	.005	.006	.004	----	----

Of the refractories available for use in the ceramic-packed thermocouples magnesium oxide appears to have been and to continue to be the most popular. Aluminum oxide is, however, gaining favor; and beryllium, zirconium, and thorium oxides may be had on special order. The quality of and some thermal information on these refractory insulating materials is given in table 100, taken from reference [121].

The average coefficient of thermal expansion from room temperature to 700 °C of the refractory insulating materials, scaled from a chart of reference, [127] is given in table 101. Values of copper, stainless steel, and aluminum are included for comparison.

Resistivities of some ceramic insulating materials, taken from Anderson and MacKenzie's chart, are given in table 102. These data as well as

TABLE 99. *Sheath materials for ceramic-packed thermocouple stock and some of their properties*

Material	Melting point	Recommended maximum in air	Recommended		Tensile strength [d]	
			Operating atmosphere [a]	Continuous maximum temperature	at 200 °F	at 1,600 °F
Stainless steel	°F	°F		°F [a]	*psi*	*psi*
304	2,560	1,920	ORNV	1,650	68,000	----
309	----	----	ORNV	2,000	----	----
310	2,560	1,960	ORNV	2,100	87,000	23,000
316	2,280	1,760	ORNV	1,700	75,000	23,000
321	2,580	1,500	ORNV	1,600	70,000	17,000
347	2,600	1,680	ORNV	1,600	75,000	----
403	----	----	ORNV	1,650	----	----
430	----	----	ORNV	1,200	----	----
446	----	----	ORNV	2,000	----	----
Inconel	2,550	2,000	ONV [c]	2,100	93,000	5,000
Inconel X	2,620	1,500	ONV [c]	2,200	150,000	11,000
Incoloy	2,500	1,640	----	----	77,000	3,000
Hastelloy X	2,650	2,400	----	----	106,000	7,000
Hastelloy C	2,440	1,820	----	----	136,000	64,000
Haynes 25	2,420	1,820	----	----	147,000	13,000
Hastelloy F	2,400	1,620	----	----	97,000	54,000
Hastelloy B	2,240	1,400	----	----	125,000	51,000
Monel	2,460	1,640	----	----	----	----
Nionel	2,200	----	----	----	----	----
Copper	1,980	600	O [b]RNV	600	----	----
Brass	1,850	700	----	----	----	----
Aluminum	1,220	800	ORNV	700	----	----
Beryllium	2,450	400	----	----	----	----
Nichrome	2,550	2,000	----	----	----	----
Alumel	2,550	2,400	----	----	----	----
Nickel	2,647	1,500	----	----	----	----
Iron	2,791	1,000	----	----	----	----
Zircalloy	3,090	1,900	----	----	----	----
Platinum	3,216	3,000	ON [c]	3,000	----	----
Pt-Rh 10 percent	----	----	----	----	----	----
Niobium	4,379	1,600	VN	3,800	110,000	----
Molybdenum	4,750	1,000	VNR	----	137,000	30,000
Molybdenum, disilicized	4,750	3,680	----	4,400	----	----
Molybdenum, chromalized	4,750	3,400	----	----	----	----
Tantalum	5,440	750	V	5,000	96,000	22,000
Titanium	3,300	600	VN	2,000	----	----
Graphite	6,850	1,000	----	----	----	----

[a] This column is from reference [126]; symbols describing atmospheres are: O—Oxidizing; R—Reducing; N—Neutral; V—Vacuum.
[b] Scales readily in oxidizing atmosphere.
[c] Very sensitive to sulfur corrosion.
[d] After exposure to temperature of 100 hrs except for stainless steels, Haynes 25, W, Mo, Ta, and Nb.

TABLE 100. *Quality of and some thermal data on insulating materials used in ceramic-packed thermocouple stock*

Insulator	Minimum purity	Melting point	Usable temperature	Maximum equivalent boron content
	percent	°F	°F	*ppm*
Magnesia (MgO)	99.1	5,050	4,000	39
Alumina (Al_2O_3)	99.5	3,650	2,300	30
Zirconia (ZrO_2)	99.4	4,500	1,200	200 ppm of HF_2
Beryllia (BeO)	99.8	4,550	4,000	10
Thoria (ThO_2)	99.5	5,950	5,000	10

all data on thermal properties of such refractories are affected by the physical and chemical composition and history of the samples of materials studied; and so the approximate nature of such information must be kept in mind.

When used in packed stock, the resistance between wires and sheath of magnesia is said in reference 128 to be "upwards of 2000 megohms

TABLE 101. *Comparison of the average coefficients of thermal expansion of refractory insulating materials with those of three common metals*

Material	Coefficient of expansion × 10^5 [a]
	per °C
Copper	16.5
Stainless steels	13.9 to 16.4
Aluminum	9.6
Magnesium oxide	12.9
Beryllium oxide	8.1
Aluminum oxide	7.1 to 8.0
Zirconium oxide	4.2 to 5.2

[a] Average coefficient from room temperature to 700 °C.

TABLE 102. *Electrical resistivities of ceramic insulating materials*

Material	Resistivity, ohm-cm, at temperatures, °C, of					
	900	1,000	1,100	1,200	1,300	1,400
Alumina, 100%	1.3×10^8	1.8×10^7	4.6×10^5	1.5×10^5	4.7×10^5	2.5×10^5
Alumina, 99%	7.3×10^5	2.0×10^5	6.7×10^4	2.2×10^4	6.4×10^3	1.4×10^3
Beryllia	3.4×10^6	4.5×10^5	1.2×10^5	4.7×10^4	2.1×10^4	1.0×10^4
Magnesia	1.7×10^5	3.4×10^5	8.5×10^4	2.6×10^4	6.7×10^3	6.4×10^2

per foot of length at 68F temperature." Reference [123] gives "Minimum insulation resistance wire to wire, or wire to sheath is 1.5 megohms at 500 volts D.C. in sizes .062" diameter and larger for lengths to 30 feet."

Thermal conductivities of alumina, magnesia, and beryllia are, among refractories, relatively high. Actual values would have no significance here though, because not enough data on the physical properties such as density, grain size, degree of sintering, etc. are available.

Pressure tightness and porosity are properties of the made-up stock for which no generally acceptable criteria have yet evolved. Some suppliers advertise that their assemblies will stand high pressures; and they will, in the sense that the stock is not destroyed or damaged under these conditions. "Gas-tightness" of the packed ceramic is difficult to attain, however, and this is recognized by some suppliers who carry special sealing materials to apply to either the hot or cold end to attain tightness.

Porosity which is related to "gas-tightness" is of importance in uses where substances may permeate the ceramic packing and produce undesirable effects such as partially short-circuiting the thermocouple wires or by leaving corrosive agents in contact with the wires or sheath. This too is alleviated to some extent by sealers.

4. Conclusion

The information presented herein has been obtained from various sources, and is believed to provide a fairly complete coverage of the field. Obviously more information could have been given, but time and space set limitations that could not be ignored. Unfortunately, some sources of information appeared too late to be used to advantage here, but they are listed in the bibliography, and probably are available to those interested.

The search for data to include in this paper has revealed a paucity of information on some materials, particularly several just now coming into use. More knowledge concerning the properties of these materials is needed in order to utilize them to best advantage in thermocouple thermometry.

Acknowledgment is made to G. F. Blackburn and C. Halpern for their assistance in reviewing this paper, to Mr. Halpern also for his support in conducting the necessary library research, and to Mrs. B. De Wane for her patience in typing and retyping the manuscript and for arranging it in its proper form. Although the list of those who contributed material for this paper in answer to a questionnaire cannot be given, their cooperation and generosity nevertheless are highly appreciated as contributing to a more nearly complete coverage of the field.

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6. Appendix

The tables given in this section are for thermocouples for which no NBS reference tables have been heretofore available. Of these, the data for the iridium 40 percent-rhodium 60 percent versus iridium and the platinum 85 percent-iridium 15 percent versus palladium thermocouples were obtained at the National Bureau of Standards and have been presented elsewhere in expanded form as reference tables. Data for the other thermocouples which appear to be in current use, and for which data have not been obtained at the National Bureau of Standards, are presented as given in the sources cited.

TABLE 1–A. *Condensed calibration for the platinum 70 percent rhodium 30 percent versus platinum 94 percent rhodium 6 percent thermocouple*

Temperature		Emf	Temperature		Emf
°C	°F	mv	°C	°F	mv
0	32	0.000	900	1,652	3.969
25	77	0.007	1,000	1,832	4.83
50	122	0.020	1,100	2,012	5.79[1]
100	212	0.056	1,200	2,192	6.81[1]
200	392	0.162	1,300	2,372	7.89[0]
300	572	0.419	1,400	2,552	9.000
400	752	0.790	1,500	2,732	10.130
500	932	1.245	1,600	2,912	11.260
600	1,112	1.796	1,700	3,092	12.390
700	1,292	2.442	1,750	3,182	12.955
800	1,472	3.162			

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The values in this table, and mentioned in the text, are for the Ir 40% - Rh 60% vs Ir thermocouple and so should be compared with the values of table 2-A. The following values* should be substituted in table 7-A.

Temperature °F	Temperature °C	Emf mv	Temperature °F	Temperature °C	Emf mv
32	0	0	2000	1093.3	6.000
200	93.3	0.342	2200	1204.4	6.586
400	204.4	0.864	2400	1315.6	7.159
600	315.6	1.468	2600	1426.7	7.726
800	426.7	2.119	2800	1537.8	8.291
1000	537.8	2.792	3000	1648.9	8.862
1200	648.9	3.469	3200	1760.0	9.444
1400	760.0	4.131	3400	1871.1	10.040
1600	871.1	4.775	3600	1982.2	10.653
1800	982.2	5.397	3800	2093.3	11.284

*From Table 3 of Reference Tables for Thermocouples of Iridium-Rhodium Alloys Versus Iridium, G. F. Blackburn and F. R. Caldwell, J. Research NBS, C. Engineering and Instrumentation Vol. 68C, No. 1, 41-59 (Jan.-Mar. 1964).

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TABLE 2–A. *Condensed reference table for the iridium 40 percent rhodium 60 percent versus iridium thermocouple*

Temperature		Emf	Temperature		Emf
°F	°C	mv	°F	°C	mv
32	0	0	1,900	1037.8	5.513
50	10.0	0.032	2,000	1093.3	5.814
100	37.8	0.126	2,100	1148.9	6.114
150	65.6	0.227	2,200	1204.4	6.491
200	93.3	0.337	2,300	1260.0	6.708
300	148.9	0.576	2,400	1315.6	7.005
400	204.4	0.840	2,500	1371.1	7.305
500	260.0	1.122	2,600	1426.7	7.607
600	315.6	1.418	2,700	1482.2	7.914
700	371.1	1.726	2,800	1537.8	8.228
800	426.7	2.041	2,900	1593.3	8.545
900	482.2	2.361	3,000	1648.9	8.862
1,000	537.8	2.684	3,100	1704.4	9.182
1,100	593.3	3.009	3,200	1760.0	9.508
1,200	648.9	3.332	3,300	1815.6	9.839
1,300	704.4	3.654	3,400	1871.1	10.176
1,400	760.0	3.973	3,500	1926.7	10.522
1,500	815.6	4.287	3,600	1982.2	10.879
1,600	871.1	4.599	3,700	2037.8	11.243
1,700	926.7	4.907	3,800	2093.3	11.610
1,800	982.2	5.211			

TABLE 3–A. *Thermal emf of iridium 40 percent rhodium 60 percent versus copper and of copper versus iridium*

Temperature		Ir 40-Rh 60	Iridium
°F	°C	emf, mv	emf, mv
32	0	0	0
50	10.0	0.026	0.006
75	23.9	.064	.014
100	37.8	.103	.023
150	65.6	.178	.049
200	93.3	.253	.084
250	121.1	.325	.129
300	148.9	.392	.184
400	204.4	.525	.315
500	260.0	.637	.485

The iridium-rhodium is positive to copper; copper is positive to iridium

TABLE 4–A. *Condensed reference table for the platinum 85 percent iridium 15 percent versus palladium thermocouple*

Temperature		Emf	Temperature		Emf
°F	°C	mv	°F	°C	mv
32	0	0	1,200	648.9	17.054
50	10.0	0.179	1,300	704.4	18.947
80	26.7	0.437	1,400	760.0	20.910
100	37.8	0.702	1,500	815.6	22.939
150	65.6	1.254	1,600	871.1	25.033
200	93.3	1.830	1,700	926.7	27.190
300	148.9	3.051	1,800	982.2	29.403
400	204.4	4.346	1,900	1,037.8	31.670
500	260.0	5.705	2,000	1,093.3	33.985
600	315.6	7.130	2,100	1,148.9	36.342
700	371.1	8.619	2,200	1,204.4	38.732
800	426.7	10.172	2,300	1,260.0	41.141
900	482.2	11.787	2,400	1,315.6	43.569
1,000	537.8	13.470	2,500	1,371.1	46.022
1,100	593.3	15.228	2,550	1,398.9	47.255

TABLE 5–A. *Thermal emf of platinum 85 percent-iridium 15 percent versus copper and of copper versus palladium*

Temperature		Pt 85–Ir 15	Palladium
°F	°C	emf, mv	emf, mv
32	0	0.000	0.000
80	26.7	.177	.312
100	37.8	.251	.453
150	65.6	.431	.823
200	93.3	.606	1.224
250	121.1	.775	1.654
300	148.9	.938	2.116
400	204.4	1.237	3.108
500	260.0	1.502	4.201

The platinum-iridium is positive to copper; copper is positive to palladium.

The values in the table are as determined, and some differences exist between the sum of the emfs here and the values of table 4–A. Reasons for these differences are not apparent, but use of the above data will introduce no appreciable errors at higher temperatures.

TABLE 6–A. *Condensed calibration data for Geminol P and N thermocouple*

Temperature		Emf	Temperature		Emf
°F	°C	mv	°F	°C	mv
32	0	0.00	1,100	593.3	17.11
50	10.0	.24	1,200	648.9	19.05
80	26.7	.63	1,300	704.4	21.06
100	37.8	.90	1,400	760.0	23.10
150	65.6	1.58	1,500	815.6	25.20
200	93.3	2.26	1,600	871.1	27.30
300	148.9	3.66	1,700	926.7	29.46
400	204.4	5.07	1,800	982.2	31.65
500	260.0	6.57	1,900	1,037.8	33.86
600	315.6	8.18	2,000	1,093.3	36.08
700	371.1	9.84	2,100	1,148.9	38.32
800	426.7	11.56	2,200	1,204.4	40.54
900	482.2	13.35	2,300	1,260.0	42.76
1,000	537.8	15.20			

TABLE 7–A. *Calibration data for iridium 60 percent-rhodium 40 percent versus iridium thermocouple* [a]

Temperature		Emf	Temperature		Emf
°F	°C	mv	°F	°C	mv
32	0	0.00	2,000	1,093.3	5.76
200	93.3	0.32	2,200	1,204.4	6.36
400	204.4	0.82	2,400	1,315.6	6.95
600	315.6	1.39	2,600	1,426.7	7.54
800	426.7	2.00	2,800	1,537.8	8.14
1,000	537.8	2.62	3,000	1,648.9	8.77
1,200	648.9	3.26	3,200	1,760.0	9.42
1,400	760.0	3.90	3,400	1,871.1	10.09
1,600	871.1	4.53	3,600	1,982.2	10.78
1,800	982.2	5.15			

[a] The values of table 7-A are from reference [122].

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